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1 Source and age of dissolved and gaseous carbon in a peatland-riparian-stream continuum: a dual isotope ( $^{14}\text{C}$   
2 and  $\delta^{13}\text{C}$ ) analysis

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21  
22 Abstract

23 Radiocarbon isotopes are increasingly being used to investigate the age and source of carbon released from  
24 peatlands. Here we use combined  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurements to determine the isotopic composition of soil and  
25 soil decomposition products (dissolved organic carbon (DOC),  $\text{CO}_2$  and  $\text{CH}_4$ ) in a peatland-riparian-stream  
26 transect, to establish the isotopic signature and potential connectivity between carbon pools. Sampling was  
27 conducted during two time periods in 2012 to investigate processes under different temperature, hydrological  
28 and flux conditions. Isotopic differences existed in the peatland and riparian zone soil organic matter as a result  
29 of the riparian depositional formation. The peatland had a mean radiocarbon age of  $551 \pm 133$  years BP, with  
30 age increasing with depth, and  $\delta^{13}\text{C}$  values consistent with C3 plant material as the primary source. In contrast  
31 the riparian zone had a much older radiocarbon age of  $1055 \pm 107$  years BP and showed no age/depth  
32 relationship;  $\delta^{13}\text{C}$  in the riparian zone was also consistent with C3 plant material. With the exception of DOC in  
33 September, soil decomposition products were predominately  $>100\%$  modern with  $^{14}\text{C}$  values consistent with  
34 derivation from organic matter fixed in the previous 5 years. Emissions of  $\text{CO}_2$  and  $\text{CH}_4$  from the soil surface  
35 were also modern. In contrast,  $\text{CO}_2$  and  $\text{CH}_4$  evaded from the stream surface was older ( $\text{CH}_4$ : 310-537 years BP,  
36  $\text{CO}_2$ : 36 years BP to modern) and contained a more complex mix of sources combining soil organic matter and  
37 geogenic carbon. The results suggest considerable vertical transport of modern carbon to depth within the soil  
38 profile. The importance of modern recently fixed carbon and the differences between riparian and stream

39 isotopic signatures suggests that the peatland (not the riparian zone) is the most important source of carbon to  
40 stream water.

41

42 Keywords: Aquatic export, Carbon, Peatland, Riparian zone, Radiocarbon, <sup>13</sup>C

43

44 1 Introduction

45 Peatlands are an important global carbon store, containing around one third of total soil carbon, despite only  
46 covering 2-3 % of the land surface (Gorham, 1991; Turunen et al. 2002). Future climatic and anthropogenic  
47 changes have the potential to alter the ability of peatlands to store carbon by modifying both land-atmosphere  
48 and aquatic export pathways. It is therefore important to understand the current sources, ages and proportions of  
49 each carbon species in order to predict the impacts of future change scenarios (Billett et al. 2010). The net  
50 ecosystem carbon balance (NECB) of a peatland is a function of the net ecosystem exchange (NEE) of CO<sub>2</sub>  
51 between the ground surface and the atmosphere, the emission of CH<sub>4</sub> and downstream export (Chapin et al.  
52 2006). Downstream carbon export consists of particulate and dissolved organic and inorganic carbon (POC,  
53 DOC, DIC), and dissolved CO<sub>2</sub> and CH<sub>4</sub> plus vertical evasion of CO<sub>2</sub> and CH<sub>4</sub> from the water surface to the  
54 atmosphere (Billett and Harvey 2013; Limpens et al. 2008). To date, much of the focus has been on land-  
55 atmosphere exchange, but due to the importance of headwater streams in carbon release at both catchment and  
56 regional scales (Cole et al. 2007), the aquatic pathway has now been recognised as an important component of  
57 the NECB accounting for 31-51 % of uptake via NEE (Dinsmore et al. 2010; Nilsson et al. 2008; Roulet et al.  
58 2007). For example, at Auchencorth Moss, a temperate peatland in SE Scotland, the mean annual aquatic carbon  
59 export over the period 2007-2011 was 35.6 g C m<sup>-2</sup> yr<sup>-1</sup>, dominated by downstream losses of DOC (19.3 g C m<sup>-2</sup>  
60 yr<sup>-1</sup>) and CO<sub>2</sub> evasion (10.0 g C m<sup>-2</sup> yr<sup>-1</sup>) (Dinsmore et al. 2013).

61 The concentration, speciation and isotopic composition of carbon in stream waters is the result of terrestrial and  
62 aquatic carbon inputs, interactions with geological and atmospheric sources, and processing and transformations  
63 within the stream channel (Striegl et al. 2007). In many northern hemisphere peatland headwaters in-stream  
64 aquatic carbon production is limited by low temperature, low pH and short stream residence times (Dawson et  
65 al. 2001) resulting in stream water organic carbon being predominately of terrestrial origin. The terrestrial soil  
66 carbon pool, consisting of soil organic matter, DOC, CO<sub>2</sub> and CH<sub>4</sub>, is heterogeneous, particularly with depth,  
67 due to differences in production and transport mechanisms. The composition of the terrestrial carbon pool and

68 connectivity between the pools and the stream channel are the dominant controls on the concentration and  
69 speciation of carbon within headwater streams (Fiebig et al. 1990; Vidon et al. 2010; Dinsmore et al. 2008). In  
70 stable peatlands the carbon cycle is likely to be dominated by relatively modern carbon with older carbon stored  
71 at depth (Moore et al. 2013). The isotopic signature of carbon released from peatlands is therefore an indicator  
72 of the dominant carbon cycling processes and peatland stability (Moore et al. 2013).

73 Recent methodological advances have overcome many of the limitations of isotopic methods; principally the  
74 relatively large sample volumes required for  $^{14}\text{C}$  analysis and the low carbon concentrations and flux rates found  
75 in natural systems. Methods now exist for analysis of both  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  in soil, soil  $\text{CO}_2$ ,  $\text{CH}_4$  and DOC (Garnett  
76 et al. 2011), soil emitted  $\text{CO}_2$  and  $\text{CH}_4$  (Garnett et al. 2012b), stream water DOC and  $\text{CO}_2$  and  $\text{CH}_4$  evaded from  
77 the stream surface (Garnett et al. 2012c).

78 Soil  $^{14}\text{C}$  age has been found to increase with depth down the soil profile, due to peat depositional processes,  
79 from modern in near-surface layers to several thousands of years BP at depth (Charman et al. 1999; Clymo and  
80 Bryant 2008; Palmer et al. 2001). The decomposition of these soils under either oxic or anoxic conditions,  
81 depending on water table conditions, produces DOC,  $\text{CO}_2$ , and  $\text{CH}_4$ . Again these generally show an increasing  
82 age-depth profile from modern to 4330 year B.P for  $\text{CO}_2$  and modern to 3960 years BP for  $\text{CH}_4$ ; both gases  
83 being generally  $^{14}\text{C}$  enriched relative to the surrounding peat (Charman et al. 1999; Chasar et al. 2000; Clymo  
84 and Bryant 2008; Garnett et al. 2011). Similarities in the age profiles of the different carbon species are  
85 considered a sign of derivation from a similar source, namely soil organic matter (Clymo and Bryant 2008).

86 To our knowledge, only four previous studies have analysed the  $^{14}\text{C}$  content of  $\text{CH}_4$  emitted from the peatland  
87 surface. Three give values in the range of 111 to 123 %modern, although these are limited to North America  
88 (Chanton et al. 1995; Quay et al. 1991; Wahlen et al. 1989). Combined with  $\delta^{13}\text{C}$  values between -56 and -73.5  
89 ‰ they indicate a significant component of recently fixed, bacterially produced  $\text{CH}_4$ . Recent work by Garnett et  
90 al. (2012b) found  $^{14}\text{C}$  depleted  $\text{CH}_4$  from a Scottish peatland in the range 84.69 to 97.89 %modern (1399 to 195  
91 years BP), which may indicate a component of older, deep peat derived  $\text{CH}_4$ . Although  $^{14}\text{C}$  values >100  
92 %modern indicate that there is a significant component of carbon fixed since ~AD 1955, it does not preclude a  
93 component of carbon fixed pre-bomb (before ~AD 1955). Surface respiration is therefore likely to be a complex  
94 mix of multiple end members including soil and plant respiration, plant-mediated transport of older  $\text{CO}_2$  and  
95  $\text{CH}_4$  from deeper in the peat and  $^{13}\text{C}$  enriched sources, such as the weathering of carbonate material within the  
96 soil (Garnett and Hardie 2009; Hardie et al. 2009).

97 Gaseous carbon dissolved in stream water was found to be <100 %modern in the range 707-1210 years BP in  
98 the Black Burn draining Auchencorth Moss (the peatland studied here), with a strong correlation between age  
99 and discharge with younger carbon released during periods of higher flow (Garnett et al. 2012a). Peatland  
100 headwater streams have consistently been found to be supersaturated in CO<sub>2</sub> and CH<sub>4</sub> relative to the atmosphere  
101 (Hope et al. 2001; Kling et al. 1991). This, combined with the turbulent nature of these streams, results in  
102 significant evasion from the stream surface (Billett and Harvey 2013; Billett and Moore 2008; Jones and  
103 Mulholland 1998). Evaded CO<sub>2</sub> from Auchencorth Moss was found in the range ~850-1450 years BP (Billett et  
104 al. 2006) and from other catchments from modern to 1450 years BP (Billett et al. 2007) with the source of this  
105 evaded carbon representing a mix of soil derived, geogenic and atmospheric carbon. To date, the only study to  
106 measure the <sup>14</sup>C age of CH<sub>4</sub> evaded from peatland streams is Garnett et al. (2012c). Evaded CH<sub>4</sub> (1617-1987  
107 years BP) was found to be considerably older than CO<sub>2</sub> (303-521 years BP); suggesting CH<sub>4</sub> was derived from  
108 deeper horizons within the peat profile compared to CO<sub>2</sub>.

109 DOC has been found in the soil carbon pool ranging from modern to 6970 years BP (Chasar et al. 2000; Clymo  
110 and Bryant 2008; Chanton et al. 2008). Despite this, DOC in peatland headwater streams has been shown to be  
111 primarily modern and derived principally from the decomposition of recently fixed organic matter (Billett et al.  
112 2007; Mayorga et al. 2005; Schiff et al. 1997). However, some degraded systems release old carbon into the  
113 stream channel in both gaseous and dissolved forms (Frey and Smith, 2005; Guo and Macdonald 2006; Moore  
114 et al. 2013).

115 Peatland vegetation, which uses the C<sub>3</sub> photosynthetic pathway, results in soil and DOC from soil  
116 decomposition having δ<sup>13</sup>C values in the range ~ -25 to -30 ‰, although Clymo and Bryant (2008) found a  
117 narrower range between -26.2 ‰ at the surface to -27.3‰ at 7 m depth. The anaerobic decay of soil organic  
118 matter produces <sup>13</sup>C depleted CH<sub>4</sub> and <sup>13</sup>C enriched CO<sub>2</sub> relative to the source material (Hornibrook et al. 2000;  
119 Waldron et al. 1999). Garnett et al. (2011) found δ<sup>13</sup>C values of CO<sub>2</sub> increased with depth from -12.4 ‰ at 25  
120 cm depth to +8.3 ‰ at 4 m. By contrast the CH<sub>4</sub> δ<sup>13</sup>C values were in the range -58.4 ‰ to -70.6 ‰. The δ<sup>13</sup>C  
121 values when combined with <sup>14</sup>C give a clearer understanding of the decomposition processes occurring within  
122 peatlands while providing a means of identifying the sources of exported carbon.

123 Most of the studies above, with the exception of Palmer et al. (2001), have focused only on the central areas of  
124 peatland bodies, where peat deposits are thickest and most stable. However, it is changes in riparian zones, at  
125 the interface between the terrestrial and aquatic systems, which are likely to have the greatest impact on stream

126 water isotopic composition. Riparian zones, as the final area of soil that water passes through before becoming  
127 surface runoff (Burt, 2005) have a key role in controlling the hydrological response of the catchment (McGlynn  
128 and McDonnell, 2003) and the movement of water and solutes across the terrestrial-aquatic interface (Fiebig et  
129 al. 1990; Lyon et al. 2011). Stream-riparian linkages are reciprocal with streams causing erosion, flooding and  
130 sediment deposition on riparian zones, especially during periods of high flow (Luke et al. 2007; Naiman and  
131 Décamps 1997). These characteristics, combined with the redox conditions, result in the riparian zone being a  
132 dynamic and complex environment capable of transforming biochemical cycles, including carbon (Ranalli and  
133 Macalady 2010; Vidon et al. 2010). In agricultural systems, riparian zones have been found to be hotspots for  
134 denitrification, acting as a significant buffer for nitrate transport between the terrestrial and aquatic systems  
135 (Naiman and Décamps 1997). Despite the importance of riparian zones, their role in the production, transport  
136 and transformation of carbon between the terrestrial and aquatic systems in peatlands has received little  
137 attention.

138 To our knowledge this is the first time isotope techniques have been used to examine the role that the riparian  
139 zone in peatlands plays in determining stream water composition. The study combines  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  analysis of  
140 the terrestrial peatland and riparian carbon pools and soil-atmosphere emissions, with the aquatic carbon export  
141 and emission pathways to test the following hypotheses:

- 142 1. The isotopic composition of soil organic matter, DOC,  $\text{CO}_2$  and  $\text{CH}_4$  are distinct in riparian and peat soils,  
143 related to differences in the soil depositional processes and the cycling of carbon.
- 144 2.  $\text{CO}_2$ ,  $\text{CH}_4$  and DOC within stream water have a similar isotopic signature to the riparian zone, indicating the  
145 importance of the riparian zone as a source for stream export.
- 146 3. Soil emissions and stream export are composed predominately of modern carbon, indicating that overall the  
147 peatland is stable and processing recently fixed carbon.

148

## 149 2 Methods

### 150 2.1 Site Description

151 Auchencorth Moss is a 3.4 km<sup>2</sup> low lying (250-300 m above sea level), ombrotrophic peatland catchment  
152 situated 17 km south of Edinburgh, UK (55°47'34N; 3°14'35W) (Dinsmore et al. 2010). Bedrock consists of

153 upper Carboniferous/lower Devonian sandstones with thin bands of limestone and coal horizons (Billett et al.  
154 2004). These are overlain by fluvio-glacial, clay/silt-rich material, which in turn are overlain by peat deposits  
155 (<0.5 m to 5 m thick) with increasing proportions of organo-mineral soils towards the catchment outlet (Billett  
156 et al. 2004). Vegetation across the catchment is dominated by grasses and sedges (*Deschampsia flexuosa*,  
157 *Molinia caerulea*, *Festuca ovina*, *Eriophorum angustifolium*, *Eriophorum vaginatum* and *Calluna vulgaris*)  
158 covering a moss layer composed predominately of *Sphagnum* and *Polytrichum* spp. (Drewer et al. 2010). The  
159 distinctive vegetation of the riparian zone is largely dominated by *Juncus effusus* associated with a moss-rich  
160 base layer. Auchencorth Moss is predominantly used for low density (less than one livestock unit per hectare)  
161 sheep grazing throughout the year (Drewer et al. 2010). Historic, >100 year old, regularly spaced drainage  
162 ditches are present but are largely overgrown and terminate approximately 20 m before the start of the riparian  
163 zone.

164 For the purposes of this study the riparian zone is defined as a 1-5 m wide corridor immediately adjacent to the  
165 stream channel which is periodically inundated by the stream and easily identifiable by a break in slope (~ 80  
166 cm below the level of the surrounding peat). The riparian zone is characterised by distinctive soil and vegetation  
167 types and has higher than average water tables. The soils within the riparian zone contain re-worked peat inter-  
168 bedded with cm scale sand/clay horizons deposited during periods of overbanking (details below).

169 The catchment is drained by the Black Burn, a small (mean width 68 cm; Billett and Harvey 2013), turbulent,  
170 first order stream with low pH (mean pH 5.5) which displays a flashy response to rainfall events. Daily mean  
171 discharge at the catchment outlet ranges between 0.95 and 1815 L s<sup>-1</sup> with a median of 25.9 L s<sup>-1</sup> (Dinsmore et  
172 al. 2013).

173 Previous studies at the site have characterised the isotopic composition of DOC and CO<sub>2</sub> dissolved in stream  
174 water and CO<sub>2</sub> evasion from the stream surface (Billett et al. 2006, 2007; Garnett et al. 2012c). Garnett and  
175 Billett (2007) analysed the isotopic composition of riparian plants, but these are the first soil samples collected  
176 at the site.

## 177 2.2 Field procedures

178 Sampling was carried out during two campaigns in 2012, 5<sup>th</sup> April - 3<sup>rd</sup> May and 22<sup>nd</sup> August - 18<sup>th</sup> September  
179 with the sampling periods hereafter referred to as 'April' and 'September' respectively. The two time periods  
180 were chosen to represent contrasting seasons with April having cool, low productivity and dry antecedent

181 conditions, whilst in September temperatures were higher, with greater catchment productivity and wet  
182 antecedent conditions (Table 1). All sampling was carried out along a 10 m long transect connecting the  
183 peatland, riparian zone and stream sampling points (Figure 1).

184 Soil cores were collected in both the peatland and riparian zone using a 6 cm diameter gouge type soil auger.  
185 Five × 5 cm thick slices were taken from each core for isotope analysis. Both peatland and riparian cores were  
186 sampled at depths of 5-10 cm, 25-30 cm, 45-50 cm and 65-70 cm; the deepest sampling point for the peatland  
187 and riparian cores were 145-150 cm and 75-80 cm, respectively, representing the depth of transition between the  
188 peat and underlying fluvio-glacial material. The sampling depths were selected to best capture each of the  
189 identified soil horizons from soil pits which were dug in both the peatland and riparian zones. From each  
190 identified horizon soil was collected in triplicate 100 cm<sup>3</sup> metal rings to determine soil bulk density, carbon  
191 content and pH.

192 Probes for sampling soil gases consisted of a length of stainless steel tubing (outer diameter 6 mm) with a 5 cm  
193 long sampling window covered by a gas permeable, hydrophobic membrane (Accurel PP V8/2 HF, Membrana  
194 GmbH, Germany) and were installed within both the peatland and riparian zone following the method of Garnett  
195 et al. (2011). A total of 4 probes were installed at both sites comprising three replicate probes with sampling  
196 windows at a depth of 40-45 cm, and one probe with a sampling window at 65-70 cm (Figure 1). Probes were  
197 installed two weeks prior to sample collection so the small probe headspace volume (<8.8 mL) would become  
198 equilibrated with the soil. For sample collection, glass flasks (volume ~215 ml) evacuated to a high vacuum  
199 (<10<sup>-2</sup> mB) were attached to the ends of the stainless steel probes via PVC tubing (Tygon, Fisher, UK). Flasks  
200 were left in place for four weeks. Due to probe failure only two shallow riparian CO<sub>2</sub> and CH<sub>4</sub> replicates were  
201 collected in April.

202 Soil water for DOC analysis was collected from a sampling probe installed in the shallow and deep depths of  
203 both the peatland and riparian zone. The design was similar to that of the gas probes but instead of the gas  
204 permeable, hydrophobic membrane the sampling window consisted of a number of small incisions made into the  
205 stainless steel tubing to allow water ingress. Glass vacuum flasks were only deployed for a period of 24 hours  
206 for soil water collection.

207 Samples of CO<sub>2</sub> and CH<sub>4</sub> emitted from the peatland and riparian surface were collected from static chambers  
208 following the method of Garnett et al (2012b). Chamber design was based on that of Dinsmore et al. (2009) and  
209 Drewer et al. (2010). A chamber was installed in the peatland and riparian zone each consisting of an opaque

210 polypropylene flange (40 cm diameter) inserted into the ground to a depth of approximately 15 cm; chamber  
211 bases were installed seven weeks prior to sampling and left *in-situ* for the duration of the study. Extension  
212 sections of 25 cm height, made from the same opaque polypropylene as the bases, were placed onto the bases  
213 and the chambers closed with a solid metal lid. Two auto shutoff Quick Coupling sampling points were installed  
214 in the chamber lid (Colder Products Company, USA) with one used for sample collection and the other opened  
215 to the atmosphere to equilibrate pressure within the chamber during sampling. Chamber volumes were 32 L and  
216 50 L for peatland and riparian zone, respectively.

217 Static chambers were closed for a period of 5-9 days to allow sufficient concentrations of CO<sub>2</sub> and CH<sub>4</sub> to build  
218 up. For routine <sup>14</sup>C analysis a minimum sample size of ~1 mg C was required. Using this value the minimum  
219 concentration within the chamber and required sample volume were calculated. CH<sub>4</sub> concentration was the  
220 limiting factor due to fluxes being considerably lower than for CO<sub>2</sub>. Changes in chamber CO<sub>2</sub> and CH<sub>4</sub>  
221 concentrations over the enclosure period were monitored by periodically collecting and analysing 100 ml  
222 subsamples by gas chromatography at CEH Edinburgh. When chamber CH<sub>4</sub> concentration reached 100 ppmv  
223 gas samples were collected in 10 L foil bags (SKC Ltd, UK) using a battery powered pump with a flow rate of  
224 ~1 L min<sup>-1</sup>. To collect sufficient sample in the riparian zone in April, when concentrations stabilised at 25 ppmv,  
225 five foil bags were collected over a series of days to prevent over extraction of the chamber volume and the  
226 drawing up of soil gases.

227 To collect the gas evaded from the stream surface a floating chamber was installed on the Black Burn (Garnett  
228 et al. 2012c). The floating chamber (surface area ~1,500 cm<sup>2</sup>, volume 42 L) was constructed from the bottom  
229 section of a barrel ('Open top keg', Ampulla Ltd, UK). To increase the buoyancy a ring of plastic and pipe  
230 lagging was placed around the chamber at water level. The chamber was secured in place using two, 1.5 m  
231 length (10 mm diameter) stainless steel rods secured into the stream bed. The chamber was connected to these  
232 rods using stainless steel saddle clamps (RS Components, UK) to allow it to rise and fall with changes in stream  
233 level. The chamber was installed and allowed to equilibrate for 24 hours prior to sampling. An auto shutoff  
234 Quick Coupling sampling point on the top of the chamber allowed the removal of chamber gas to a foil gas bag  
235 using a pump as described above (a second sampling point was opened during sampling to act as a vent by  
236 which atmospheric equilibrium was maintained). Stream water DOC was collected by filling a 300 ml glass  
237 bottle.

238 2.3 Laboratory procedures

239 The outer 1 cm of the soil core sections was removed before processing to avoid potential contamination from  
240 smearing of peat material from higher in the soil profile during sampling. The remaining soil sample was then  
241 homogenised and a sub-sample sent to the NERC Radiocarbon Facility (RCF) for further analysis. No pre-  
242 treatment to remove mobile fractions from the soil was carried out. The soil was dried and then combusted to  
243 CO<sub>2</sub> using an elemental analyser and converted to graphite by Fe/Zn reduction (Slota et al. 1987).

244 Soil was analysed for dry bulk density by drying for 24 hours at 106 °C. Samples were then combusted for 16  
245 hours at 375 °C to determine the %organic carbon content by loss on ignition (Ball, 1964). Soil pH was  
246 measured in a mixture of two parts deionised water to one part fresh peat using a MP220 pH meter (Mettler  
247 Toledo, UK).

248 The glass flasks containing the soil atmosphere samples and the foil gas bags containing the chamber samples  
249 were returned to the RCF and separated into their CO<sub>2</sub> and CH<sub>4</sub> components. The glass flask samples were  
250 separated using the method of Garnett et al. (2011). Firstly the CO<sub>2</sub> component was trapped on a molecular  
251 sieve cartridge with the remaining CO<sub>2</sub>-free CH<sub>4</sub> sample combusted to CO<sub>2</sub> by passing over platinum-  
252 aluminium beads at 950 °C in an atmosphere of excess oxygen. The CH<sub>4</sub> derived CO<sub>2</sub> was then cryogenically  
253 purified using a slush trap (mix of dry ice and ethanol at -78 °C) to remove water and then liquid nitrogen (-196  
254 °C) to separate CO<sub>2</sub> from other gases. Finally the CO<sub>2</sub> sample was recovered from the molecular sieve cartridge  
255 by heating (500 °C) while attached to a vacuum rig (Garnett and Murray, 2013). For the foil bags a subsample  
256 of the contents was taken and the CO<sub>2</sub> component isolated by cryogenic purification. The CH<sub>4</sub> component was  
257 isolated from the remaining sample as described for the flask samples above.

258 Water samples were filtered through 0.7 µm GF/F filter papers (Whatman, UK), which had been pre-combusted  
259 at 500 °C for 5 hours prior to use (Chanton et al. 2008). Samples were returned to clean glass bottles and stored  
260 in the dark at 4 °C before being passed to the RCF. Each sample was then acidified to pH 4 and sparged with N<sub>2</sub>  
261 gas for 20 mins. After the pH had been returned to pH 7 a measured volume was removed for rotary  
262 evaporation. After freeze drying the sample was converted to CO<sub>2</sub> by combustion in an elemental analyser and  
263 converted to graphite by Fe/Zn reduction (Slota et al. 1987).

264 For each sample, δ<sup>13</sup>C (relative to the Vienna Pee Dee Belemnite standard) was determined on a dual inlet  
265 isotope ratio mass spectrometer (Thermo Fisher Delta V). In the five instances where there was insufficient  
266 sample for a separate δ<sup>13</sup>C measurement (\* in Appendix 1) this was performed by AMS at the same time as <sup>14</sup>C  
267 measurement. <sup>14</sup>C was determined at the Scottish Universities Environmental Research Centre (SUERC)

268 accelerator mass spectrometry (AMS) facility. Results are reported following radiocarbon conventions as both  
269 %modern and conventional radiocarbon age (years BP) where applicable, with  $\pm 1\sigma$  analytical precision and  
270 were normalised to a  $\delta^{13}\text{C}$  of -25 ‰ to account for mass-dependent fractionation. The five samples requiring  
271 ‘small sample’ AMS analysis have a greater analytical uncertainty for both  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  (Appendix 1).

## 272 2.4 Data analysis

273 As no attempt was made to remove atmospheric  $\text{CO}_2$  or  $\text{CH}_4$  from the chambers prior to sampling, a mass  
274 balance approach was used to remove their contribution to the isotope results. For  $\text{CO}_2$  the assumed atmospheric  
275 composition in the chamber prior to sampling was 390 ppmv with a  $^{14}\text{C}$  concentration of 103.7 %modern and  
276  $\delta^{13}\text{C}$  of -9 ‰ (Levin et al. 2008). Atmospheric  $\text{CH}_4$  was removed from the  $\text{CH}_4$  isotope results assuming a  
277 concentration of 2 ppmv, a  $^{14}\text{C}$  content of 130 %modern and a  $\delta^{13}\text{C}$  of -47 ‰ (Lassey et al. 2007).

278 Where data from the replicate samples ( $n=3$ ) have been summarised the arithmetic mean and the standard error  
279 of the mean were calculated. To test for statistical differences between peatland and riparian zones a Student’s t-  
280 test was performed for the soil profiles and ANOVA to test for differences in the soil gas replicates. The  
281 standard deviation was also calculated for the replicates to determine the precision of the results.

282 An isotope mass balance approach (Equation 1) (Chaser et al. 2000) was used to estimate the fraction ( $f$ ) of  
283 carbon from different sources within samples of soil DOC,  $\text{CO}_2$  and  $\text{CH}_4$  and evasion  $\text{CO}_2$  and  $\text{CH}_4$ .  $\Delta^{14}\text{C}_{\text{meas}}$  is  
284 the measured  $^{14}\text{C}$  content of the sample and  $\Delta^{14}\text{C}_{\text{mod}}$  is the atmospheric  $^{14}\text{C}$  content of carbon fixed by plants  
285 during 2012 estimated at 103.7 %modern (Levin et al. 2008). To estimate the contribution from soil ( $\Delta^{14}\text{C}_{\text{soil}}$ ),  
286 measured  $^{14}\text{C}$  values from this study were used. To determine the fraction of geogenic derived carbon from  
287 bedrock sources,  $\Delta^{14}\text{C}_{\text{geo}}$  value of 0 %modern (i.e. of sufficient age that no measureable  $^{14}\text{C}$  remains) was used  
288 in place of  $\Delta^{14}\text{C}_{\text{soil}}$ .

289 Equation 1 
$$\Delta^{14}\text{C}_{\text{meas}} = (f)(\Delta^{14}\text{C}_{\text{mod}}) + (1 - f)(\Delta^{14}\text{C}_{\text{soil}})$$

290 Local meteorological data over the full year 2012 were provided from the European Monitoring and Evaluation  
291 Programme (EMEP) flux tower located ~1 km from the transect and were used to aid the interpretation of  
292 results. Data on background carbon concentrations and fluxes and hydrological conditions including water table,  
293 soil water temperature and stream discharge are from Leith et al. (in prep).

294

## 295 3 Results

### 296 3.1 Hydrology and meteorology

297 Total rainfall for 2012 was 1237 mm, 7 % higher than the 2002 - 2008 average of 1055 mm (Drewer et al. 2010)  
298 but with an uneven distribution across the year (Leith et al. in prep); 32 % of the total annual rainfall fell in June  
299 and July. In the April sampling period there was a total of 90.1 mm of rainfall with a lower total of 78.4 mm in  
300 September. Average air temperature during the September sampling period was 11.1 °C compared with 4.9 °C  
301 in April; stream water temperature was also higher during the September sampling period (Table 1). Average  
302 water table depths in the peatland were the same in both sampling periods (-30 cm) but with a larger range in  
303 April (-60 to -7 cm) compared to September (-47 to -8 cm). Water tables were higher in the riparian zone with  
304 means of -17 cm in April and -22 cm in September (Figure 2). Greater rainfall in April meant that mean  
305 discharge was greater ( $42.0 \text{ L s}^{-1}$ ) compared to September ( $25.3 \text{ L s}^{-1}$ ) (Table 1). However, when samples for  
306 DOC and evasion  $\text{CO}_2$  and  $\text{CH}_4$  were collected stream discharge was relatively stable and similar ( $11.3$  and  $13.9$   
307  $\text{L s}^{-1}$ , respectively).

308 Antecedent conditions in the three months prior to sampling varied considerably between the two periods. In  
309 April the preceding three months were characterised by dry weather with low discharge whereas in September  
310 the three months before sampling were extremely wet with consistently high discharge. A number of  
311 overbanking events occurred throughout the year, shown by above ground surface water table positions in the  
312 riparian zone (Figure 2). The two largest of these, which occurred in the summer period between the two  
313 sampling occasions, flooded the entire riparian zone with noticeable amounts of stream sediment, consisting of  
314 peat and sandy material, deposited onto the surface of the riparian zone.

### 315 3.2 Soil

316 Peatland and riparian soil profiles differed despite the two sites being only 10 m apart (Figure 3). The peatland  
317 profile contained five organic horizons (O1-5) with varying levels of decomposition. Two horizons (O2, O4)  
318 contained abundant poorly decomposed graminoid plant fragments, while horizons O3 and O5 were  
319 characterised by highly humified peat. The O2 and O4 horizons contained the most abundant plant fragments  
320 and had lower bulk density,  $0.10$  and  $0.11 \text{ g cm}^{-3}$ , compared with the more humified horizons O3 and O5. The  
321 organic carbon content of the soil was relatively low (30.7-39.3 %) suggesting a component of mineral soil  
322 within the peat (Table 2).

323 The riparian profile contained three organic horizons (O1-3) with a continuous sand layer (C1) at 60 cm  
324 marking the boundary between the overlying peat and a deeper horizon with broken and contorted sandy lenses  
325 (C2), which in turn overlaid the fluvio-glacial horizon (Figure 3). The transition was also marked by a large  
326 increase in the bulk density from 0.14-0.35 g cm<sup>-3</sup> in the organic horizons to 0.86 g cm<sup>-3</sup> in the sand-rich horizon  
327 (Table 2). This horizon contained much less organic carbon (5.2 %), compared with organic layers above (18.1  
328 to 28.4 %). All horizons in the riparian zone contained less organic material compared to the peatland where  
329 organic carbon content ranged from 30.7-39.3 %C; soil pH was also lower in the peatland soils (Table 2). The  
330 irregular decrease in carbon content with depth and the presence of sandy horizons are characteristic of fluvisols  
331 (Figure 3).

332 In both the peat and riparian zone soils the O1 horizon was poorly decomposed and contained abundant roots  
333 and plant litter. The extent of this layer and the composition of the plant material varied between the sites with  
334 graminoid remains in the peatland and a thicker layer of *Juncus effusus* roots in the riparian zone. Active rooting  
335 depth was ~25 cm in both soil types.

336 Peatland soil age increased with depth from 134 ± 37 years BP at 5-10 cm depth (O1-O2 horizons) to 665 ± 37  
337 years BP at the basal depth (O5) (Figure 4, with details in Appendix 1). The age at 25-30 cm (O3) did not fit this  
338 age-depth profile, being considerably older at 947 ± 41 years BP. The riparian soil profile was significantly  
339 older than the peat (T= -2.95 P= 0.02) ranging from 759 ± 37 years BP at 25-30 cm depth (O2) to 1407 ± 36  
340 years BP at 65-70 cm depth (C2). Neither the peatland nor riparian zone soil profiles displayed a linear increase  
341 in age with depth, which is typical in most peats. No significant differences existed in peatland and riparian  
342 δ<sup>13</sup>C, with all values in the range of -26.7 to -29.9 ‰.

### 343 3.3 Porewater DOC, CO<sub>2</sub> and CH<sub>4</sub>

344 DOC, CO<sub>2</sub> and CH<sub>4</sub> in peatland porewater were consistently >100 % modern (Figure 5) (Appendix 1). The  
345 riparian zone also had <sup>14</sup>C values predominantly >100 % modern, but with three exceptions. Aged CH<sub>4</sub> was  
346 found at 70 cm in the riparian zone in April (81 ± 77 years BP) with riparian porewater DOC in September  
347 having a radiocarbon age of 327 ± 37 years BP at 45 cm depth and 117 ± 37 years BP at 70 cm depth. Porewater  
348 DOC, CO<sub>2</sub> and CH<sub>4</sub> were all significantly younger than the surrounding soil material; which at equivalent  
349 depths were 459 ± 37 and 552 ± 35 years BP in the peatland and 933 ± 37 and 1407 ± 36 years BP in the  
350 riparian zone.

351 Across the sampling periods,  $\delta^{13}\text{C}$  values for porewater  $\text{CO}_2$  had mean values of -7.4 ‰ in the deep peat and -14  
352 ‰ in the deep riparian zone, whereas porewater  $\text{CH}_4$  had mean values of -76.4 and -73.2 ‰ in the peatland and  
353 riparian zone, respectively.  $\text{CO}_2$  was enriched in  $^{13}\text{C}$  and  $\text{CH}_4$  depleted in  $^{13}\text{C}$ , relative to soil material which  
354 ranged from -26.7 to -29.9 ‰.  $\delta^{13}\text{C}$  values for porewater DOC had a narrower range in April (-27.5 to -28.2 ‰)  
355 and September (-27.6 to -27.9 ‰).  $^{14}\text{C}$  concentrations were similar between the different carbon species but the  
356 wider range of  $^{13}\text{C}$  values resulted in different carbon species having distinct clusters (Figure 5).

357 No significant differences occurred in the  $^{14}\text{C}$  content of porewater  $\text{CO}_2$  or  $\text{CH}_4$  between the peatland and  
358 riparian zone in either April or September. Significant differences existed in April for both  $\delta^{13}\text{CH}_4$  ( $F=16.5$ ,  
359  $P<0.05$ ) and  $\delta^{13}\text{CO}_2$  ( $F=198$ ,  $P<0.01$ ) with the riparian porewater  $^{13}\text{C}$  depleted in both  $\text{CH}_4$  and  $\text{CO}_2$  relative to  
360 the peatland. In September there were no significant differences between the peatland and riparian porewater for  
361 either  $\delta^{13}\text{CH}_4$  or  $\delta^{13}\text{CO}_2$ . There was good agreement between the three replicates of  $^{14}\text{CO}_2$  in the peatland with  
362 mean  $\pm$  standard deviation of  $103.66 \pm 0.46$  %modern and  $104.58 \pm 0.81$  %modern in April and September,  
363 respectively. There was greater variability in the riparian zone with values of  $104.51 \pm 1.63$  %modern (April)  
364 and  $103.17 \pm 1.58$  %modern (September).

### 365 3.4 Soil surface emissions

366 Gaseous carbon emissions from the surface of the soil were all  $>100$  %modern (Figure 6, Appendix 1).  $\text{CO}_2$   
367 emissions from the peatland were enriched in  $^{14}\text{C}$  (104.79 and 105.70 %modern in April and September) relative  
368 to the contemporary atmosphere (103.7 %modern in 2012) while the riparian emissions were depleted (100.59  
369 and 100.99 %modern in April and September). Based on comparisons with the atmospheric  $^{14}\text{CO}_2$  record of  
370 Levin et al. 2008, the  $^{14}\text{CO}_2$  results suggest that  $\text{CO}_2$  emitted from the peatland surface in 2013 was on average  
371 fixed from the atmosphere between about 2007 and 2010.

372 Emitted  $\text{CH}_4$  was consistently more enriched in  $^{14}\text{C}$  from the peatland (107.29 and 108.25 %modern in April and  
373 September) than the riparian zone (101.79 and 104.84 %modern). Overall, emissions in both the peatland and  
374 riparian zone were more  $^{14}\text{C}$  enriched in September than April. All emissions were significantly enriched  
375 relative to the age of soil material which at 5-10 cm depth had radiocarbon ages of  $134 \pm 37$  and  $1107 \pm 37$  years  
376 BP in the peatland and riparian zone, respectively.

377  $\delta^{13}\text{C}$  values for  $\text{CO}_2$  emitted from the peatland and riparian zone had a narrow range (-25.9 to -27.1‰) with  
378 values more depleted in September than April (Figure 6).  $\text{CH}_4$  had a larger range of  $\delta^{13}\text{C}$  values across the

379 measurement periods between -63.2 and -58.0 ‰ (peatland) and -75.9 and -63.5 ‰ (riparian).  $\delta^{13}\text{C}_{\text{CH}_4}$  values  
380 were more enriched in September than April, the opposite pattern found for  $\text{CO}_2$  (above).

### 381 3.5 Stream evasion and DOC export

382 Evasion was depleted in  $^{14}\text{C}$  relative to soil emissions suggesting a contribution from aged carbon. Evaded  $\text{CO}_2$   
383 had radiocarbon values of  $36 \pm 37$  years BP and modern and evaded  $\text{CH}_4$  was aged 537 and  $310 \pm 38$  years BP  
384 in April and September respectively (Appendix 1). Evaded  $\text{CO}_2$  in April (-17.4 ‰) was  $^{13}\text{C}$ -enriched compared  
385 to September (-20.5 ‰).  $\text{CH}_4$  was  $^{13}\text{C}$ -depleted, with values of -58.1 ‰ and -54.3 ‰ in April and September  
386 respectively (Figure 6).

387 Stream water DOC showed the largest range in  $^{14}\text{C}$  ranging from 100.41 % modern in April to 106.47 % modern  
388 in September. The more enriched value in September was opposite to the pattern seen for soil DOC. No  
389 significant differences were seen in  $\delta^{13}\text{C}$ , with values of -28.7 ‰ in both sampling periods (Figure 6).

## 390 4 Discussion

### 391 4.1 Composition of terrestrial carbon pools

392 The composition and depth of the soil profiles were considerably different in the peatland and riparian zone  
393 (Figure 3). Riparian soils were characterised by sandy horizons (C1 and C2 horizons), higher bulk density and  
394 an irregular decrease in % C with depth (Table 2) indicating the deposition of eroded and reworked peat and  
395 mineral material during periods of overbanking. Dense vegetation on the surface of the riparian zone is likely to  
396 contribute to the trapping of sediment transported by flood waters (Evans and Warburton 2005). The complete  
397 vegetation cover will also minimise the erosion of soil horizons; suggesting that deposition rather than erosion is  
398 creating the riparian soil profile. Despite the peatland being only 10 m from the stream, it is approximately 80  
399 cm higher than the adjacent riparian zone and whilst the riparian zone was inundated on several occasions  
400 during this study, no flood events high enough to reach the peatland were recorded in the period July 2011 to  
401 February 2013.

402 The soil isotopic data showed the riparian zone to be considerably older (759-1407 years BP) than the peatland  
403 (134-947 years BP) (Figure 4), possibly reflecting the input of older stream sediment from overbanking events.  
404 This is in agreement with Palmer et al. (2001), the only other study we are aware of to determine the isotopic

405 composition of both peatland and riparian soils. The  $\delta^{13}\text{C}$  values cover a narrow range from -26.7 to -29.9 ‰  
406 indicating C3 plant material was the primary source of carbon in both peatland and riparian soils.

407 No clear age/depth relationship was observed in the riparian zone (Figure 4) highlighting the complexity of  
408 riparian zone soil formation. In the peatland profile,  $^{14}\text{C}$  age increased with depth (with the exception of the  
409 point at 25 cm depth) and our data suggest a high peat accumulation rate. The anomalous age at 25-30 cm depth  
410 could be due to the deposition of soot particles (Charman and Garnett 2005), historical additions of soil  
411 improvement materials containing  $\text{CaCO}_3$ , or a large flood event. The peatland site is also on the edge of the  
412 peatland plateau in comparison to other studies which have dated soil cores in more stable areas in the centre of  
413 the peatland (Aravena et al. 1993; Charman et al. 1999; Clymo and Bryant 2008).

414 Since it was our intention to take a snapshot of the  $^{14}\text{C}$  in the total soil C pool it was not appropriate to perform a  
415 pre-treatment of the soil samples, as would normally be undertaken when deriving a chronological record using  
416 radiocarbon analysis. As a result, mobile fractions would have been included within the samples, as would the  
417 presence of any mineral soil material, especially carbonates or coal fragments. The high apparent accumulation  
418 rate is likely to be a result of the composition of the peat, which contains poorly decomposed graminoid plant  
419 material to a depth of 80 cm, plus the transport of young mobile fractions, such as root exudates or DOC, down  
420 the soil profile.

421 Soil gases in both the peatland and riparian zone were generally >100 % modern;  $\text{CO}_2$  ranged from 100.73 to  
422 105.66 % modern and  $\text{CH}_4$  from 99.00 to 105.46 % modern, with values becoming more  $^{14}\text{C}$  depleted with depth.  
423 The results are in agreement with other studies which measured the isotopic composition of soil gases in  
424 peatlands, with modern  $\text{CO}_2$  found at 30 cm (Billett et al. 2012) and modern  $\text{CH}_4$  at 50 cm depth (Clymo and  
425 Bryant 2008). Only one sample (deep riparian  $\text{CH}_4$  in April), was <100 % modern. This contrasts with other  
426 studies which have widely found aged carbon at depth, with  $\text{CO}_2$  98.79-94.58 % modern at 50-100 cm depth  
427 (Billett et al. 2012; Clymo and Bryant 2008) and  $\text{CH}_4$  97.30-77.30 % modern at 25-100 cm depth (Garnett et al.  
428 2011).

429 Consistent with other studies (Charman et al. 1999; Clymo and Bryant 2008, Chanton et al. 2008) soil gases  
430 were consistently younger than the surrounding soil material at both sampling depths in both the riparian zone  
431 and the peatland. Isotope mass balance indicates that soil organic matter only contributed 1-5 % of  $\text{CO}_2$  and  $\text{CH}_4$   
432 at 40-45 cm rising to 5-24 % at 65-70 cm. The remainder is likely to be derived from recently fixed carbon  
433 derived from either the downward transport of young  $\text{CO}_2$  and  $\text{CH}_4$  from the surface or infiltration of DOC

434 down the soil profile providing the substrate for fermentation and methanogenesis (Aravena et al. 1993; Corbett  
435 et al. 2013). The similarity in  $^{14}\text{C}$  ages between  $\text{CO}_2$  and  $\text{CH}_4$  suggests derivation from a single source, namely  
436 DOC transport down the soil profile (Clymo and Bryant 2008; Garnett et al. 2011).

437 Porewater DOC, with the exception of the riparian zone in September, was >100 % modern. Modern DOC at  
438 shallow depths has been found across a range of other peatlands (Chaser et al. 2000; Chanton et al. 2008) with  
439 transport of plant derived DOC from the surface down the soil profile shown to be the main process responsible  
440 for the presence of modern DOC at depth (Corbett et al. 2013). In September, the riparian zone displayed an age  
441 reversal with  $^{14}\text{C}$  ages of  $327 \pm 37$  years BP at 40-45 cm depth and  $117 \pm 37$  years BP at 65-70 cm depth. The  
442 isotope mass balance indicated a 52 % contribution from soil at the shallow and 26 % at the deeper depths.  
443 During the three months prior to the September sampling period there were a large number of storm events  
444 (Figure 2), leading to overbanking and inundation of the riparian zone. During these events, peat and sandy  
445 material, most likely soil organic matter eroded from upstream areas, was deposited onto the surface of the  
446 riparian zone. We suggest that DOC was leached from this deposited peat material and transported vertically  
447 within the soil profile, explaining the presence of aged DOC in the riparian zone in September. While a number  
448 of storm events occurred in the three months preceding the April sampling period, none were sufficiently large  
449 to result in noticeable sediment deposition. This suggests that with the exception of large storm events, DOC is  
450 sourced predominantly from modern recently fixed carbon.

451  $\delta^{13}\text{C}$  values for both  $\text{CO}_2$  and  $\text{CH}_4$  were significantly different between the peatland and riparian zone sites in  
452 April but not in September. Differences in the methanogenic pathway ( $\text{CO}_2$  reduction or acetate fermentation)  
453 calculated from carbon isotope fractionation ( $\alpha\text{C}$ ), calculated using the method of Whiticar et al. (1986), are  
454 reflected in values >1.065 indicating  $\text{CO}_2$  reduction and values <1.055 indicating acetate fermentation (Conrad  
455 2005). Peatland values (Table 3) were consistent with  $\text{CO}_2$  reduction (average 1.072 across all samples) and  
456 were similar to the value of 1.075 found by Clymo and Bryant (2008). However, the riparian zone in September  
457 had lower  $\alpha\text{C}$  values with two points suggesting a greater contribution from acetate fermentation as found in a  
458 number of other peatlands (Charman et al. 1999). It has been suggested by Sugimoto and Wada (1993) that  
459 acetate fermentation uses more labile carbon than  $\text{CO}_2$  reduction (Chanton et al. 2008). Two potential processes  
460 responsible could be the input of labile root exudates at the end of the growing season in September associated  
461 with *Juncus effusus*, which was only found in the riparian zone, or the addition of carbon to the surface of the

462 riparian zone between April and September when overbanking occurred. Again this highlights the important role  
463 of stream processes in biogeochemical cycling within the riparian zone.

464 High analytical costs limit the number of samples that can be analysed for  $^{14}\text{C}$  and restricts sample replication.  
465 Where replication has been included in studies (e.g. Clymo and Bryant 2008) variability between replicates of  
466 soil decomposition products has generally been small. This study, which was carried out in the dynamic peat  
467 margin and riparian zone also found good agreement between replicates. The riparian zone had greater  
468 variability in  $^{14}\text{CO}_2$ , with higher standard deviation than the peatland. The variability in the riparian zone can in  
469 part be due to the greater proportion of riparian samples analysed by small sample AMS, which had a larger  
470 associated uncertainty (Appendix 1). The same pattern was evident for  $^{14}\text{CH}_4$  with greater variability in the  
471 riparian replicates compared with the peatland. Despite the slightly larger uncertainty in the riparian zone, the  
472 replication was generally very good across all samples highlighting the validity and reliability of the radiocarbon  
473 techniques used in this study.

#### 474 4.2 Soil surface emissions

475 Soil surface emissions of  $\text{CO}_2$  and  $\text{CH}_4$  were all  $>100\%$  modern (Figure 6) and in line with the results from  
476 other studies (Chanton et al. 1995; Quay et al. 1991; Wahlen et al. 1989; Hardie et al. 2009). Emissions from the  
477 riparian zone were consistently depleted in  $^{14}\text{C}$  relative to the peatland. The  $\delta^{13}\text{C}$  values suggested a mixture of  
478 sources combining recently fixed carbon and a component of more  $^{13}\text{C}$  depleted soil carbon. Hardie et al. (2009)  
479 partitioned total ecosystem respiration and found it to be composed of  $\sim 36\%$  soil respiration, 41-54 % from  
480 plant respiration and  $\sim 10$ -23 % from plant mediated transport from depth. Hornibrook (2009) showed that the  
481 transport mechanism between soils at  $<50$  cm depth and the surface determines the  $\delta^{13}\text{C}$  value of surface emitted  
482  $\text{CH}_4$ . Figure 7 shows that the peatland soil emissions are most likely derived from diffusive transport through  
483 pore water, while in the riparian zone there is a component of active transport through plant aerenchyma.  
484 Preferential loss of  $^{12}\text{CH}_4$  through the aerenchyma of graminoid plants results in more  $^{13}\text{C}$ -enriched  $\text{CH}_4$   
485 (Hornibrook 2009). The riparian zone in the study site contains abundant *Juncus effusus* which is known to  
486 transport  $\text{CH}_4$  through its aerenchyma facilitating transport from deeper soil layers (Dinsmore et al. 2009).  
487 Modern  $\text{CO}_2$  and  $\text{CH}_4$  were found at both sampling depths within the soil at Auchencorth Moss, suggesting that  
488 this porewater carbon is contributing to surface emissions.

489

490 The build up of CO<sub>2</sub> and CH<sub>4</sub> in the chamber headspace during the long (5-9 day) chamber closure period is  
491 likely to have had an impact on the soil-atmosphere diffusion gradient, and hence on the flux rate (Davidson et  
492 al. 2002). Over the closure period, the rate of concentration increase within the chamber began to slow after ~24  
493 hours but did not level off over the ~5 days prior to sampling. It is unlikely that the carbon isotope results were  
494 affected by this slowing of the diffusion gradient (Garnett et al. 2012b). Furthermore, given the cool mean air  
495 temperatures in April (4.9 °C) and September (11.1 °C), there was no observed vegetation die back in the  
496 chambers, which would have altered the balance of soil and plant respiration. Ebullition is unlikely to be  
497 significant at this site as soil CH<sub>4</sub> concentrations were consistently less than the minimum concentration (~8.0  
498 mg CH<sub>4</sub> L<sup>-1</sup>) required for bubble formation (Baird et al. 2004). We therefore conclude that our results are a good  
499 representation of the isotopic composition of bulk respiration from the peatland and riparian zone.

500

#### 501 4.3 Export via the aquatic pathway

502 DOC in stream water was modern but with a greater enrichment of <sup>14</sup>C in September. This finding is consistent  
503 with the results from many other studies which determined the dual isotope composition of DOC in peatland  
504 headwater streams (Billett et al. 2007, 2012; Schiff et al. 1997). In-stream processing would lead to DOC  
505 becoming more <sup>13</sup>C enriched (Billett et al. 2012), however the consistency of δ<sup>13</sup>C between the sampling periods  
506 in the stream and the similarities between soil and stream DOC, suggests there was very little in-stream  
507 processing at the site. This supports the conclusions of other studies such as Dinsmore and Billett (2008) who  
508 attributed aquatic carbon in the same study stream to allochthonous sources rather than in-stream processing.

509 Evaded CO<sub>2</sub>, which had <sup>14</sup>C values of 98.36 and 101.35 %modern, was within the range of 83.52-107.00  
510 %modern found across a range of peatland catchments (Billett et al. 2007; Garnett et al. 2012c). The results  
511 were however considerably younger than previous studies which determined the isotopic composition of evasion  
512 and dissolved CO<sub>2</sub> ~800 m downstream of the site used in this study. Billett et al. (2006) reported evasion <sup>14</sup>C  
513 ages of up to 1454 years BP, and Garnett et al. (2012a) measured dissolved CO<sub>2</sub> concentrations in the range  
514 707-1210 years BP.

515 CH<sub>4</sub> evasion was considerably older than evaded CO<sub>2</sub> with ages of 537 ± 38 years BP in April and 310 ± 38  
516 years BP in September. This was younger than the results from Garnett et al. (2012c), the only other study to  
517 measure the <sup>14</sup>CH<sub>4</sub> content of evasion, who reported ages in the range 1617-1987 years BP at another Scottish

518 peatland site. Evaded CO<sub>2</sub> and CH<sub>4</sub> were depleted in <sup>14</sup>C relative to the soil gases, which were predominantly  
519 modern, indicating contributions from an additional <sup>14</sup>C depleted source.

520 CO<sub>2</sub> from carbonate weathering and CH<sub>4</sub> from coal seams, both of which occur in the catchment bedrock  
521 (Billett et al. 2004), may contribute additional geogenic carbon. These geogenic sources will contribute to  
522 stream water via deeper hydrological flowpaths and will be <sup>14</sup>C dead (i.e. of sufficient age that no measurable  
523 <sup>14</sup>C remains). They therefore have the potential to significantly shift the isotopic signature while only  
524 contributing small amounts of carbon. Near-surface hydrological flowpaths, at similar depths to where the  
525 porewater isotopic measurements were made, were found to consist predominantly of modern, plant derived  
526 carbon (Figure 5). Mass balance using the isotopic composition of atmospheric CO<sub>2</sub> in 2012 (<sup>14</sup>C = 103.7  
527 %modern; δ<sup>13</sup>C = -9 ‰) and geogenic carbon (<sup>14</sup>C = ~0 %modern; δ<sup>13</sup>C = ~0 ‰) indicates a contribution up to  
528 5 % and 28 % for <sup>14</sup>CO<sub>2</sub> and δ<sup>13</sup>CO<sub>2</sub>, respectively, similar to the ~21 % and 30 % calculated by Billett et al.  
529 (2007). The younger radiocarbon age for CO<sub>2</sub> evasion than reported downstream (Billett et al. 2006; Garnett et  
530 al. 2012a) may therefore be explained by a lesser contribution from geogenic carbon inputs at our upstream site  
531 highlighting spatial variability in sources along the stream length. The mass balance also suggests a greater  
532 contribution from geogenic CH<sub>4</sub> sources to the isotopic composition of evasion <sup>14</sup>CH<sub>4</sub> (27 %) than for <sup>14</sup>CO<sub>2</sub> (5  
533 %). Another source of aged CH<sub>4</sub> could be deep peat derived CH<sub>4</sub>, as suggested by Garnett et al. (2012c). While  
534 measured porewater CH<sub>4</sub> was generally modern, peat up to 5 m depth occurs upstream in the catchment, which  
535 may contribute an unmeasured source of old deep peat derived CH<sub>4</sub>. The results suggest that unmeasured  
536 sources (including deeper soil carbon and geogenic inputs) are contributing to evasion but overall, modern, plant  
537 derived carbon is the predominant component.

#### 538 4.4 The role of the riparian zone

539 Differences in the soil physical properties and the <sup>14</sup>C content between the peatland and riparian zone can be  
540 linked to the deposition of reworked peat material onto the surface of the riparian zone during overbanking  
541 events. This results in the peatland and riparian zone, despite only being 10 m apart, being distinct  
542 biogeochemical environments. An increase in the frequency and intensity of storms, which is expected under  
543 current climate change predictions (Pachauri and Reisinger 2007), could lead to an increase in the rate of  
544 sediment deposition making the riparian carbon cycle particularly sensitive to climate related changes.

545 The isotope results from this study highlight some of the differences in carbon dynamics within the peat-  
546 riparian-stream continuum. The different δ<sup>13</sup>CH<sub>4</sub> signatures between the peatland and riparian areas indicate not

547 only the varying carbon dynamics involved in the production of CO<sub>2</sub> and CH<sub>4</sub> within the soil profile, but also  
548 the transport mechanism by which these gases reach the soil surface. Additionally, aged DOC was only found in  
549 the riparian zone after overbanking events occurred, suggesting that carbon within the deposited sediment is  
550 labile and readily incorporated into the soil or converted to DOC, CO<sub>2</sub> or CH<sub>4</sub>. This highlights the important role  
551 that depositional processes have on the isotopic signature of soil and soil gases within the riparian zone.

552 The results of this study suggest that deeper peat layers contribute only a small proportion to stream and soil  
553 surface emissions, unlike degraded peatlands (Moore et al. 2013). Evasion, which was the only pathway to have  
554 an isotopic signature indicating a component of aged carbon, consisted predominately of modern soil derived  
555 CO<sub>2</sub> and CH<sub>4</sub> but with a component from geogenic sources of up to 5 % for CO<sub>2</sub> and 28 % for CH<sub>4</sub>. This  
556 suggests that the stream bed may be acting as a pathway by which carbonate weathering derived CO<sub>2</sub> and deep  
557 geologically derived coal bed CH<sub>4</sub> can be released. Gaseous carbon exported via the stream is therefore a more  
558 complex mix of sources than emissions from the soil surface. Despite the aged DOC found in the riparian zone,  
559 stream water DOC was consistently modern, again suggesting that the riparian zone is not a major contributor of  
560 carbon to the stream.

561 The overall prevalence of modern carbon shows that the carbon cycle in this peatland predominately involves  
562 modern, recently fixed carbon in agreement with studies which find Auchencorth Moss to be a net sink of  
563 carbon and in an actively aggrading state (Dinsmore et al. 2010, 2013).

564

## 565 5 Conclusions

566 The soil characteristics and isotopic composition of soil and its decomposition products are distinctly different  
567 in the riparian zone and the peatland. Soil was older in the riparian zone (1055 ± 107 years BP) than in the  
568 peatland (551 ± 133 years BP). These results suggest that the deposition of stream sediment onto the riparian  
569 zone and the rapid processing of this carbon is an important carbon source to the riparian zone and is likely to be  
570 the process responsible for many of the differences observed between the peatland and riparian zone.

571 Despite the importance of hydrochemical interactions between the stream and riparian zone the relationship  
572 does not appear to be reciprocal for peatland carbon. The isotopic composition of stream water was different to  
573 that found in the riparian zone with evasion containing carbon from elsewhere in the catchment with a possible  
574 contribution from geogenic sources of up to 5 % for CO<sub>2</sub> and 28 % for CH<sub>4</sub>. Despite the aged DOC found in the

575 riparian zone in September, stream water DOC was consistently modern, again suggesting that the riparian zone  
576 is not a major contributor of carbon to the stream.

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908 **Table 1** Mean and (min – max) of water temperature (measured in either dipwells or the stream channel) and  
 909 water table depth. Discharge is the mean  $\pm$  SE as range was fixed (0.28 to 290 L s<sup>-1</sup>). Values are calculated for  
 910 April and September sampling periods and for the whole of 2012

Sampling Period	Site	Temperature (°C)	Water table (cm)	Discharge (L s <sup>-1</sup> )
April	Peatland	6.1 (6.0 – 6.3)	-30 (-59 to -6)	42.0 $\pm$ 1.3
	Riparian	5.8 (5.6 – 6.0)	-17 (-46 to +6)	
	Stream	5.5 (0.6 – 9.6)		
September	Peatland	11.5 (11.0 – 12.3)	-30 (-47 to -8)	25.3 $\pm$ 1.1
	Riparian	11.1 (10.7 – 11.4)	-22 (-47 to +46)	
	Stream	11.7 (6.7 – 16.3)		
Annual	Peatland	7.1 (3.5 – 11.4)	-31 (-90 to -2.3)	48.6 $\pm$ 0.5
	Riparian	7.1 (3.0 – 12.3)	-19 (-90 to +50)	
	Stream	6.9 (-3.9 – 25.8)		

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933 **Table 2** Soil properties for the horizons shown in Figure 3. No samples were collected from the riparian C1  
934 horizon and the peatland O1 horizon as they were too thin for sample collection  
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Soil	Horizon	Bulk density (g cm <sup>-3</sup> )	pH	% OC
Riparian	O1	0.14	4.0	28.4
	O2	0.35	4.5	18.1
	O3	0.31	4.2	26.8
	C1	/	5.3	/
	C2	0.86	5.7	5.2
Peatland	O1	/	4.0	/
	O2	0.10	3.9	30.7
	O3	0.14	3.9	33.0
	O4	0.11	4.2	39.3
	O5	0.18	4.6	34.6

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958 **Table 3**  $\alpha$ C values for the soil gases. <sup>a</sup> indicates CO<sub>2</sub> reduction and <sup>b</sup> acetate fermentation as the likely  
 959 production pathway based on Whiticar et al. (1986).  
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Site	Sample type	April $\alpha$ C	September $\alpha$ C
Peatland	Soil (40-45cm)	1.072 <sup>a</sup>	1.071 <sup>a</sup>
	Soil (40-45cm)	1.075 <sup>a</sup>	1.060 <sup>a</sup>
	Soil (40-45cm)	1.072 <sup>a</sup>	1.066 <sup>a</sup>
	Soil (65-70) cm	1.075 <sup>a</sup>	1.074 <sup>a</sup>
Riparian Zone	Soil (40-45cm)	/	1.047 <sup>b</sup>
	Soil (40-45cm)	1.073 <sup>a</sup>	1.061 <sup>a</sup>
	Soil (40-45cm)	1.078 <sup>a</sup>	1.046 <sup>b</sup>
	Soil (65-70) cm	1.066 <sup>a</sup>	1.056 <sup>a</sup>

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984 **Appendix 1** All radiocarbon data from this study. SPa-c refer to the replicates at the shallow depth in the  
 985 peatland; SRa-c refers to replicates at the shallow depth in the riparian zone. \* indicates insufficient sample  
 986 collected for routine  $^{14}\text{C}$  analysis so small sample AMS used with  $\delta^{13}\text{C}$  determined online by the AMS  
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Sample	Publication Code (SUERC-)	$^{14}\text{C}$ Enrichment (%modern $\pm 1 \sigma$ )	Radiocarbon age (years BP $\pm 1 \sigma$ )	$\delta^{13}\text{C}$ ( $\pm 0.1 \text{ ‰}$ )
Soil				
Peat (5-10 cm)	40585	98.34 $\pm$ 0.45	134 $\pm$ 37	-27.9
Peat (25-30 cm)	44328	88.88 $\pm$ 0.45	947 $\pm$ 41	-26.7
Peat (45-50 cm)	40586	94.45 $\pm$ 0.43	459 $\pm$ 37	-27.4
Peat (65-70 cm)	44329	93.36 $\pm$ 0.41	552 $\pm$ 35	-29.9
Peat (145-150 cm)	40587	92.05 $\pm$ 0.42	665 $\pm$ 37	-28.5
Riparian (5-10 cm)	40588	87.13 $\pm$ 0.40	1107 $\pm$ 37	-27.0
Riparian (25-30 cm)	44330	90.98 $\pm$ 0.42	759 $\pm$ 37	-27.6
Riparian (45-50 cm)	40589	89.03 $\pm$ 0.41	933 $\pm$ 37	-27.8
Riparian (65-70 cm)	44331	83.93 $\pm$ 0.37	1407 $\pm$ 36	-27.6
Riparian (75-80 cm)	40590	87.53 $\pm$ 0.40	1070 $\pm$ 37	-28.0
Soil CO <sub>2</sub>				
Apr - SPa - CO <sub>2</sub>	40571	103.40 $\pm$ 0.47	Modern	-12.0
Apr - SPb - CO <sub>2</sub>	40575	104.19 $\pm$ 0.48	Modern	-12.0
Apr - SPc - CO <sub>2</sub>	40577	103.39 $\pm$ 0.47	Modern	-11.0
Apr - DP - CO <sub>2</sub>	44297	102.90 $\pm$ 0.48	Modern	-7.8
Apr - SRb - CO <sub>2</sub>	40578	103.36 $\pm$ 0.47	Modern	-19.8
Apr - SRc - CO <sub>2</sub>	40579	105.66 $\pm$ 0.45	Modern	-21.0
Apr - DR - CO <sub>2</sub>	44298	101.22 $\pm$ 0.45	Modern	-15.2
Sept - SPa-CO <sub>2</sub>	44299	105.02 $\pm$ 0.49	Modern	-11.0
Sept - SPb-CO <sub>2</sub>	44300	103.65 $\pm$ 0.48	Modern	-17.4
Sept - SPc-CO <sub>2</sub>	44301	105.07 $\pm$ 0.49	Modern	-10.7
Sept - DP-CO <sub>2</sub>	44304	102.58 $\pm$ 0.45	Modern	-6.9
Sept - SRa-CO <sub>2</sub>	44305	103.36 $\pm$ 0.48	Modern	-16.0
Sept - SRb-CO <sub>2</sub>	44306	101.50 $\pm$ 0.51	Modern	-14.3
Sept - SRc-CO <sub>2</sub>	44307	104.67 $\pm$ 0.49	Modern	-17.1
Sept - DR-CO <sub>2</sub>	44308	100.73 $\pm$ 0.47	Modern	-13.2
Soil CH <sub>4</sub>				
Apr - SPa - CH <sub>4</sub>	40570	104.51 $\pm$ 0.48	Modern	-78.4
Apr - SPb - CH <sub>4</sub>	40572	104.25 $\pm$ 0.45	Modern	-81.3
Apr - SPc - CH <sub>4</sub>	40576	104.41 $\pm$ 0.45	Modern	-77.5
Apr - DP - CH <sub>4</sub>	44296	102.73 $\pm$ 0.48	Modern	-77.2
Apr - SRb - CH <sub>4</sub>	40492*	102.40 $\pm$ 0.51	Modern	-86.6
Apr - SRc - CH <sub>4</sub>	40505*	104.56 $\pm$ 0.53	Modern	-92.1
Apr - DR - CH <sub>4</sub>	46329*	99.00 $\pm$ 0.94	81 $\pm$ 77	-76.0
Sept - SPa- CH <sub>4</sub>	43509	105.46 $\pm$ 0.49	Modern	-76.9
Sept - SPb- CH <sub>4</sub>	46330*	104.78 $\pm$ 1.01	Modern	-73.0
Sept - SPc- CH <sub>4</sub>	43510	105.26 $\pm$ 0.47	Modern	-71.8
Sept - DP- CH <sub>4</sub>	43511	103.16 $\pm$ 0.48	Modern	-75.1
Sept - SRa- CH <sub>4</sub>	43514	103.04 $\pm$ 0.48	Modern	-60.5
Sept - SRb- CH <sub>4</sub>	46331*	103.71 $\pm$ 1.44	Modern	-70.7
Sept - SRc- CH <sub>4</sub>	43515	104.89 $\pm$ 0.46	Modern	-60.7
Sept - DR- CH <sub>4</sub>	43516	102.07 $\pm$ 0.48	Modern	-65.9
Chamber CO <sub>2</sub>				
Apr - Peatland- CO <sub>2</sub>	43494	104.79 $\pm$ 0.49	Modern	-25.9
Apr - Riparian -CO <sub>2</sub>	43496	100.55 $\pm$ 0.47	Modern	-26.6
Apr - Evasion - CO <sub>2</sub>	43490	98.86 $\pm$ 0.46	36 $\pm$ 37	-17.4
Sept - Peatland- CO <sub>2</sub>	43500	105.70 $\pm$ 0.49	Modern	-26.3
Sept - Riparian -CO <sub>2</sub>	43504	100.99 $\pm$ 0.47	Modern	-27.1

Sept - Evasion - CO <sub>2</sub>	43498	101.39 ± 0.45	Modern	-20.5
Chamber CH <sub>4</sub>				
Apr - Peatland- CH <sub>4</sub>	43491	107.29 ± 0.48	Modern	-63.2
Apr - Riparian - CH <sub>4</sub>	43495	101.79 ± 0.48	Modern	-75.9
Apr - Evasion - CH <sub>4</sub>	43489	93.19 ± 0.44	537 ± 38	-58.1
Sept - Peatland- CH <sub>4</sub>	43499	108.25 ± 0.50	Modern	-58.0
Sept - Riparian - CH <sub>4</sub>	43501	104.84 ± 0.49	Modern	-63.5
Sept - Evasion - CH <sub>4</sub>	43497	95.96 ± 0.45	310 ± 38	-54.3
DOC				
Apr - SP - DOC	44314	104.94 ± 0.49	Modern	-27.5
Apr - DP - DOC	44315	104.79 ± 0.49	Modern	-28.1
Apr - SR - DOC	44316	105.14 ± 0.49	Modern	-28.1
Apr - DR - DOC	44317	104.87 ± 0.46	Modern	-28.2
Apr - Stream - DOC	44318	100.41 ± 0.47	Modern	-28.7
Sept - SP - DOC	44319	102.16 ± 0.47	Modern	-27.6
Sept - DP - DOC	44320	100.42 ± 0.47	Modern	-27.7
Sept - SR - DOC	44321	96.01 ± 0.45	327 ± 37	-27.7
Sept - DR - DOC	44324	98.55 ± 0.46	117 ± 37	-27.9
Sept - Stream - DOC	44325	106.47 ± 0.49	Modern	-28.7

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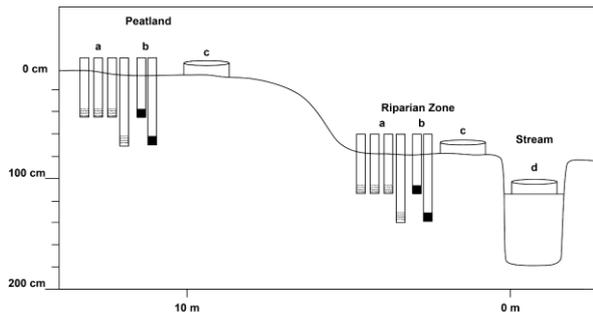
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**Fig. 1** Schematic of the transect setup used in this study. Sampling probes installed at 40 cm and 70 cm depth

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for the collection of (a) soil gases ( $\text{CO}_2$  and  $\text{CH}_4$ ) and (b) soil DOC in both the peatland and riparian zone.

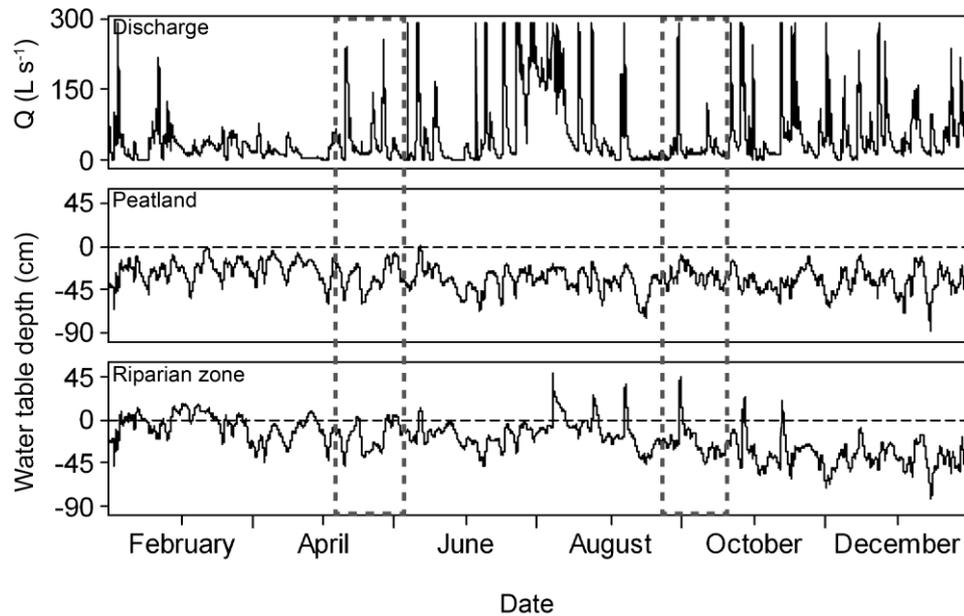
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Chambers (c) and (d) represent static chambers for the collection of soil emission  $\text{CO}_2$  and  $\text{CH}_4$ , and a floating

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chamber for the collection of evasion  $\text{CO}_2$  and  $\text{CH}_4$ , respectively

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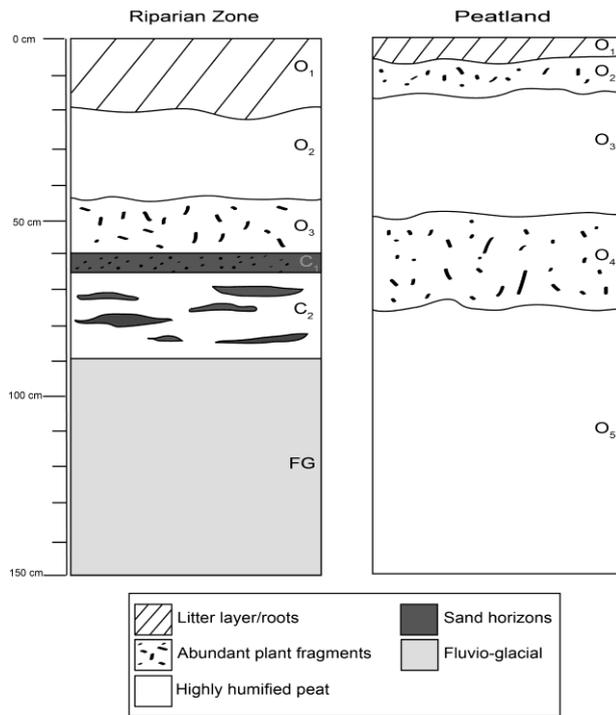
**Fig. 2** Graphs showing a) Discharge (Q), b) water table position in the peatland and c) water table position in the

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riparian zone across the full year 2012. The April and September isotope sampling periods are highlighted by

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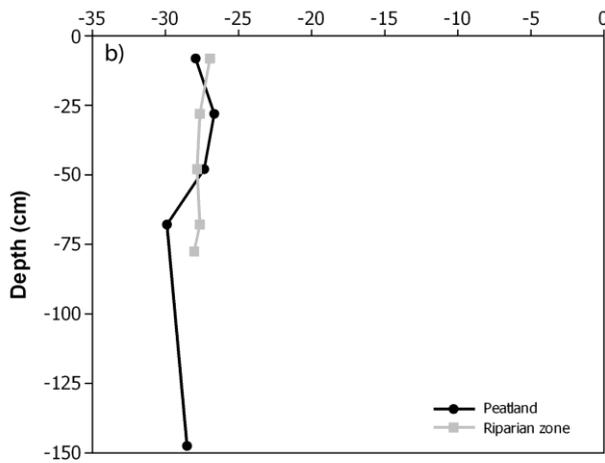
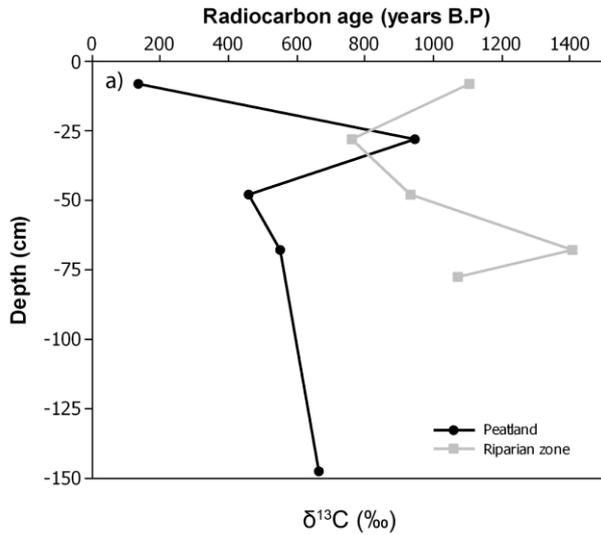
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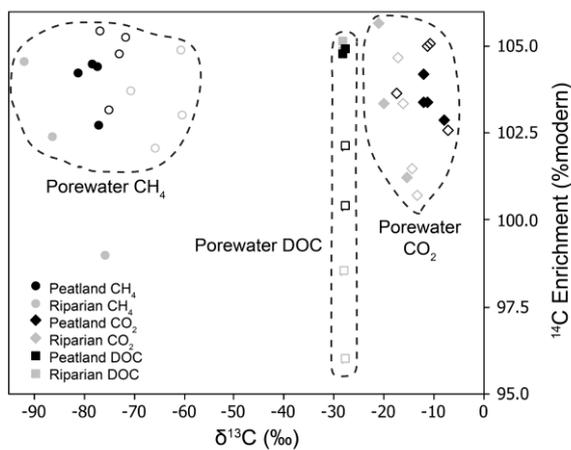
**Fig. 3** Soil profiles from 0 to 150 cm for the riparian zone and the peatland. O1, O2, O3, O4 and O5 represent organic soil horizons, C1 and C2 represent organo-mineral horizons and FG represents the underlying fluvio-glacial horizon



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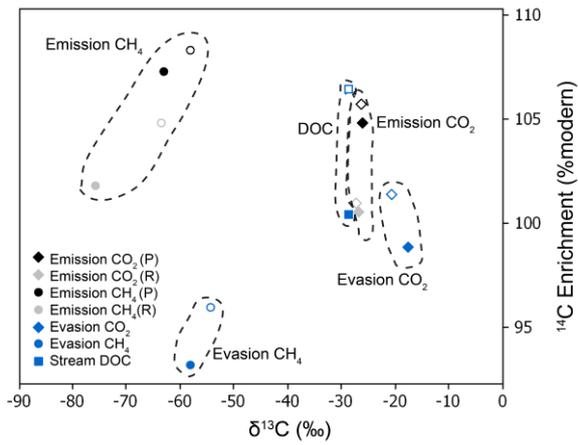
1024 **Fig. 4** Soil profiles of a) radiocarbon age (years BP) and b)  $\delta^{13}\text{C}$  (‰) in the peatland and riparian zone

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1027 **Fig. 5**  $^{14}\text{C}$  /  $\delta^{13}\text{C}$  scatterplot of porewater  $\text{CO}_2$ ,  $\text{CH}_4$  and DOC. Closed symbols represent the April sampling  
 1028 period and open symbols September. The dashed boxes highlight the clustering of the carbon species



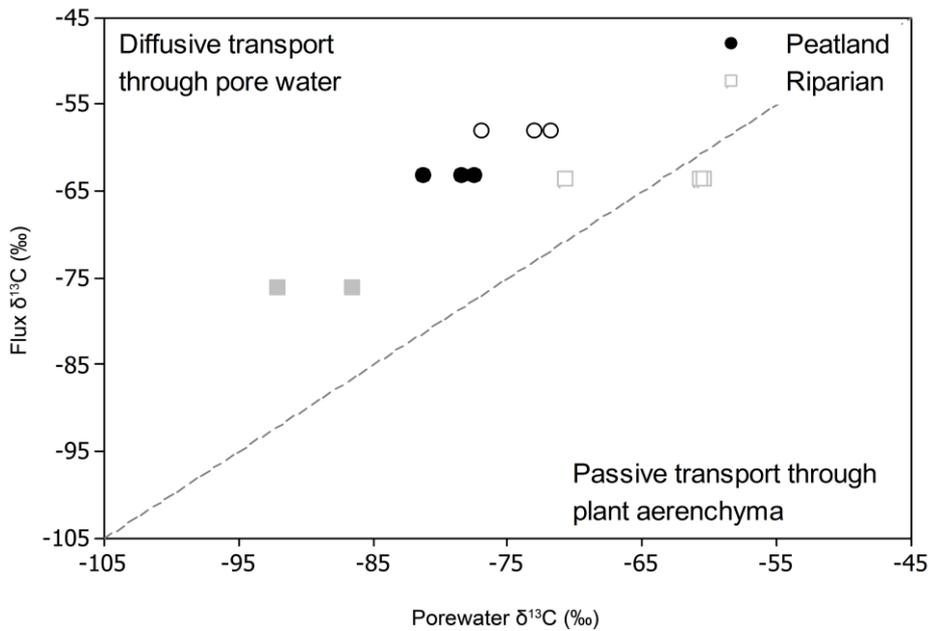
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**Fig. 6**  $^{14}\text{C} / \delta^{13}\text{C}$  scatterplot of emissions from the soil surface of the peatland (P) and riparian (R), stream evasion and lost downstream as DOC. Closed symbols represent the April sampling period and open symbols September. The dashed boxes highlight the clustering of the carbon species



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**Fig. 7** Flux pathway adapted from Hornibrook (2009). Closed symbols indicate the April period and open symbols September. The dashed 1:1 line represents transport without partitioning such as via ebullition events