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Article (refereed) - postprint

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

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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}C and δ^{13}C measurements to determine the isotopic composition of soil and

25 soil decomposition products (dissolved organic carbon (DOC), CO_2 and 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 ± 133 years BP, with

30 age increasing with depth, and δ^{13}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 ± 107 years BP and showed no age/depth

32 relationship; δ^{13}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}C values consistent with

34 derivation from organic matter fixed in the previous 5 years. Emissions of CO_2 and CH_4 from the soil surface

35 were also modern. In contrast, CO_2 and CH_4 evaded from the stream surface was older (CH_4: 310-537 years BP,

36 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.

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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_2

51 between the ground surface and the atmosphere, the emission of CH_4 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_2 and CH_4 plus vertical evasion of CO_2 and CH_4 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^{-2} yr^{-1}, dominated by downstream losses of DOC (19.3 g C m^{-2}

60 yr^{-1}) and CO_2 evasion (10.0 g C m^{-2} yr^{-1}) (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_2 and CH_4, 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}C analysis and the low carbon concentrations and flux rates found

75 in natural systems. Methods now exist for analysis of both ^{14}C and δ^{13}C in soil, soil CO_2, CH_4 and DOC (Garnett

76 et al. 2011), soil emitted CO_2 and CH_4 (Garnett et al. 2012b), stream water DOC and CO_2 and CH_4 evaded from

77 the stream surface (Garnett et al. 2012c).

78 Soil ^{14}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, CO_2, and CH_4. Again these generally show an increasing

82 age-depth profile from modern to 4330 year B.P for CO_2 and modern to 3960 years BP for CH_4; both gases

83 being generally ^{14}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}C content of 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 δ^{13}C values between -56 and -73.5

89 ‰ they indicate a significant component of recently fixed, bacterially produced CH_4. Recent work by Garnett et

90 al. (2012b) found ^{14}C depleted 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 CH_4. Although ^{14}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 CO_2 and

95 CH_4 from deeper in the peat and ^{13}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_2 and CH_4 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_2 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 ^{14}C age of CH_4 evaded from peatland streams is Garnett et al. (2012c). Evaded CH_4 (1617-1987

107   years BP) was found to be considerably older than CO_2 (303-521 years BP); suggesting CH_4 was derived from

108   deeper horizons within the peat profile compared to CO_2.

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 C3 photosynthetic pathway, results in soil and DOC from soil

116   decomposition having $\delta^{13}C$ 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 ^{13}C depleted CH_4 and ^{13}C enriched CO_2 relative to the source material (Hornibrook et al. 2000;

119   Waldron et al. 1999). Garnett et al. (2011) found $\delta^{13}C$ values of CO_2 increased with depth from -12.4 ‰ at 25

120   cm depth to +8.3 ‰ at 4 m. By contrast the CH_4 $\delta^{13}C$ values were in the range -58.4 ‰ to -70.6 ‰. The $\delta^{13}C$

121   values when combined with ^{14}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}C and $\delta^{13}C$ 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, CO_2 and 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. CO_2, 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^2 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^{-1} with a median of 25.9 L s^{-1} (Dinsmore et

172   al. 2013).

173   Previous studies at the site have characterised the isotopic composition of DOC and CO_2 dissolved in stream

174   water and CO_2 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, 5th April - 3rd May and 22nd August - 18th 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^3 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^{-2} 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_2 and CH_4 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_2 and CH_4 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

polypropylene flange (40 cm diameter) inserted into the ground to a depth of approximately 15 cm; chamber

bases were installed seven weeks prior to sampling and left *in-situ* for the duration of the study. Extension

sections of 25 cm height, made from the same opaque polypropylene as the bases, were placed onto the bases

and the chambers closed with a solid metal lid. Two auto shutoff Quick Coupling sampling points were installed

in the chamber lid (Colder Products Company, USA) with one used for sample collection and the other opened

to the atmosphere to equilibrate pressure within the chamber during sampling. Chamber volumes were 32 L and

50 L for peatland and riparian zone, respectively.

Static chambers were closed for a period of 5-9 days to allow sufficient concentrations of CO_2 and CH_4 to build

up. For routine ^{14}C analysis a minimum sample size of ~1 mg C was required. Using this value the minimum

concentration within the chamber and required sample volume were calculated. CH_4 concentration was the

limiting factor due to fluxes being considerably lower than for CO_2. Changes in chamber CO_2 and CH_4

concentrations over the enclosure period were monitored by periodically collecting and analysing 100 ml

subsamples by gas chromatography at CEH Edinburgh. When chamber CH_4 concentration reached 100 ppmv

gas samples were collected in 10 L foil bags (SKC Ltd, UK) using a battery powered pump with a flow rate of

~1 L min^{-1}. To collect sufficient sample in the riparian zone in April, when concentrations stabilised at 25 ppmv,

five foil bags were collected over a series of days to prevent over extraction of the chamber volume and the

drawing up of soil gases.

To collect the gas evaded from the stream surface a floating chamber was installed on the Black Burn (Garnett

et al. 2012c). The floating chamber (surface area ~1,500 cm^2, volume 42 L) was constructed from the bottom

section of a barrel ('Open top keg', Ampulla Ltd, UK). To increase the buoyancy a ring of plastic and pipe

lagging was placed around the chamber at water level. The chamber was secured in place using two, 1.5 m

length (10 mm diameter) stainless steel rods secured into the stream bed. The chamber was connected to these

rods using stainless steel saddle clamps (RS Components, UK) to allow it to rise and fall with changes in stream

level. The chamber was installed and allowed to equilibrate for 24 hours prior to sampling. An auto shutoff

Quick Coupling sampling point on the top of the chamber allowed the removal of chamber gas to a foil gas bag

using a pump as described above (a second sampling point was opened during sampling to act as a vent by

which atmospheric equilibrium was maintained). Stream water DOC was collected by filling a 300 ml glass

bottle.

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_2 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_2 and CH_4 components. The glass flask samples were

250 separated using the method of Garnett et al. (2011). Firstly the CO_2 component was trapped on a molecular

251 sieve cartridge with the remaining CO_2-free CH_4 sample combusted to CO_2 by passing over platinum-

252 aluminium beads at 950 °C in an atmosphere of excess oxygen. The CH_4 derived CO_2 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_2 from other gases. Finally the CO_2 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_2 component isolated by cryogenic purification. The CH_4 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_2

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_2 by combustion in an elemental analyser and

263 converted to graphite by Fe/Zn reduction (Slota et al. 1987).

264 For each sample, $\delta^{13}C$ (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 $\delta^{13}C$ measurement (* in Appendix 1) this was performed by AMS at the same time as ^{14}C

267 measurement. ^{14}C was determined at the Scottish Universities Environmental Research Centre (SUERC)

9

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 ±1σ analytical precision and

270   were normalised to a $\delta^{13}C$ 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}C and $\delta^{13}C$ (Appendix 1).

272   2.4 Data analysis

273   As no attempt was made to remove atmospheric CO_2 or CH_4 from the chambers prior to sampling, a mass

274   balance approach was used to remove their contribution to the isotope results. For CO_2 the assumed atmospheric

275   composition in the chamber prior to sampling was 390 ppmv with a ^{14}C concentration of 103.7 %modern and

276     $\delta^{13}C$ of -9 ‰ (Levin et al. 2008). Atmospheric CH_4 was removed from the CH_4 isotope results assuming a

277   concentration of 2 ppmv, a ^{14}C content of 130 %modern and a $\delta^{13}C$ 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, CO_2 and CH_4 and evasion CO_2 and CH_4. $\Delta^{14}C_{meas}$ is

284   the measured ^{14}C content of the sample and $\Delta^{14}C_{mod}$ is the atmospheric ^{14}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 ($\Delta^{14}C_{soil}$),

286   measured ^{14}C values from this study were used. To determine the fraction of geogenic derived carbon from

287   bedrock sources, $\Delta^{14}C_{geo}$ value of 0 %modern (i.e. of sufficient age that no measureable ^{14}C remains) was used

288   in place of $\Delta^{14}C_{soil.}$

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

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 L s^{-1}) compared to September (25.3 L s^{-1}) (Table 1). However, when samples for

306 DOC and evasion CO_2 and CH_4 were collected stream discharge was relatively stable and similar (11.3 and 13.9

307 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 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^{-3} in the organic horizons to 0.86 g cm^{-3} 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     $\delta^{13}C$, with all values in the range of -26.7 to -29.9 ‰.

343   3.3 Porewater DOC, CO_2 and CH_4

344   DOC, CO_2 and CH_4 in peatland porewater were consistently >100 %modern (Figure 5) (Appendix 1). The

345   riparian zone also had ^{14}C values predominantly >100 %modern, but with three exceptions. Aged CH_4 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_2 and CH_4 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, $\delta^{13}C$ values for porewater CO_2 had mean values of -7.4 ‰ in the deep peat and -14

352 ‰ in the deep riparian zone, whereas porewater CH_4 had mean values of -76.4 and -73.2 ‰ in the peatland and

353 riparian zone, respectively. CO_2 was enriched in ^{13}C and CH_4 depleted in ^{13}C, relative to soil material which

354 ranged from -26.7 to -29.9 ‰. $\delta^{13}C$ values for porewater DOC had a narrower range in April (-27.5 to -28.2 ‰)

355 and September (-27.6 to -27.9 ‰). ^{14}C concentrations were similar between the different carbon species but the

356 wider range of ^{13}C values resulted in different carbon species having distinct clusters (Figure 5).

357 No significant differences occurred in the ^{14}C content of porewater CO_2 or CH_4 between the peatland and

358 riparian zone in either April or September. Significant differences existed in April for both $\delta^{13}CH_4$ (F=16.5,

359 P<0.05) and $\delta^{13}CO_2$ (F=198, P<0.01) with the riparian porewater ^{13}C depleted in both CH_4 and CO_2 relative to

360 the peatland. In September there were no significant differences between the peatland and riparian porewater for

361 either $\delta^{13}CH_4$ or $\delta^{13}CO_2$. There was good agreement between the three replicates of $^{14}CO_2$ in the peatland with

362 mean ± standard deviation of 103.66 ± 0.46 % modern and 104.58 ± 0.81 % modern in April and September,

363 respectively. There was greater variability in the riparian zone with values of 104.51± 1.63 % modern (April)

364 and 103.17 ± 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). CO_2

367 emissions from the peatland were enriched in ^{14}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 $^{14}CO_2$ record of

370 Levin et al. 2008, the $^{14}CO_2$ results suggest that CO_2 emitted from the peatland surface in 2013 was on average

371 fixed from the atmosphere between about 2007 and 2010.

372 Emitted CH_4 was consistently more enriched in ^{14}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}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 ± 37 and 1107 ± 37 years

376 BP in the peatland and riparian zone, respectively.

377 $\delta^{13}C$ values for 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). CH_4 had a larger range of $\delta^{13}C$ values across the

379 measurement periods between -63.2 and -58.0 ‰ (peatland) and -75.9 and -63.5 ‰ (riparian). $\delta^{13}CH_4$ values

380 were more enriched in September than April, the opposite pattern found for CO_2 (above).

381 3.5 Stream evasion and DOC export

382 Evasion was depleted in ^{14}C relative to soil emissions suggesting a contribution from aged carbon. Evaded CO_2

383 had radiocarbon values of 36 ± 37 years BP and modern and evaded CH_4 was aged 537 and 310 ± 38 years BP

384 in April and September respectively (Appendix 1). Evaded CO_2 in April (-17.4 ‰) was ^{13}C-enriched compared

385 to September (-20.5 ‰). CH_4 was ^{13}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}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 $\delta^{13}C$, 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 $\delta^{13}C$ 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}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 $CaCO_3$, 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}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; CO_2 ranged from 100.73 to

422   105.66 % modern and CH_4 from 99.00 to 105.46 % modern, with values becoming more ^{14}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 CO_2 found at 30 cm (Billett et al. 2012) and modern CH_4 at 50 cm depth (Clymo and

425   Bryant 2008). Only one sample (deep riparian CH_4 in April), was <100 % modern. This contrasts with other

426   studies which have widely found aged carbon at depth, with CO_2 98.79-94.58 % modern at 50-100 cm depth

427   (Billett et al. 2012; Clymo and Bryant 2008) and 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 CO_2 and 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 CO_2 and 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}C ages between CO_2 and 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}C ages of 327 ± 37 years BP at 40-45 cm depth and 117 ± 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 δ^{13}C values for both CO_2 and CH_4 were significantly different between the peatland and riparian zone sites in

452 April but not in September. Differences in the methanogenic pathway (CO_2 reduction or acetate fermentation)

453 calculated from carbon isotope fractionation (αC), calculated using the method of Whiticar et al. (1986), are

454 reflected in values >1.065 indicating CO_2 reduction and values <1.055 indicating acetate fermentation (Conrad

455 2005). Peatland values (Table 3) were consistent with 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 αC 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 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}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 $^{14}CO_2$, 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 $^{14}CH_4$ 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 CO_2 and 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}C relative to the peatland. The δ^{13}C values suggested a mixture of

478   sources combining recently fixed carbon and a component of more ^{13}C depleted soil carbon. Hardie et al. (2009)

479   partitioned total ecosystem respiration and found it to be composed of ~36 % soil respiration, 41-54 % from

480   plant respiration and ~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 δ^{13}C value of surface emitted

482   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 $^{12}CH_4$ through the aerenchyma of graminoid plants results in more ^{13}C-enriched CH_4

485   (Hornibrook 2009). The riparian zone in the study site contains abundant *Juncus effusus* which is known to

486   transport CH_4 through its aerenchyma facilitating transport from deeper soil layers (Dinsmore et al. 2009).

487   Modern CO_2 and 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_2 and CH_4 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_4 concentrations were consistently less than the minimum concentration (~8.0

498　mg CH_4 L^{-1}) 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 ^{14}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 ^{13}C enriched (Billett et al. 2012), however the consistency of $\delta^{13}C$ 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_2, which had ^{14}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_2 ~800 m downstream of the site used in this study. Billett et al. (2006) reported evasion ^{14}C

513　ages of up to 1454 years BP, and Garnett el al. (2012a) measured dissolved CO_2 concentrations in the range

514　707-1210 years BP.

515　CH_4 evasion was considerably older than evaded CO_2 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 $^{14}CH_4$ content of evasion, who reported ages in the range 1617-1987 years BP at another Scottish

518 peatland site. Evaded CO_2 and CH_4 were depleted in ^{14}C relative to the soil gases, which were predominantly

519 modern, indicating contributions form an additional ^{14}C depleted source.

520 CO_2 from carbonate weathering and CH_4 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 ^{14}C dead (i.e. of sufficient age that no measureable

523 ^{14}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_2 in 2012 (^{14}C = 103.7

527 %modern; $\delta^{13}C$ = -9 ‰) and geogenic carbon (^{14}C = ~0 %modern; $\delta^{13}C$ = ~0 ‰) indicates a contribution up to

528 5 % and 28 % for $^{14}CO_2$ and $\delta^{13}CO_2$, respectively, similar to the ~21 % and 30 % calculated by Billett et al.

529 (2007). The younger radiocarbon age for CO_2 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_4 sources to the isotopic composition of evasion $^{14}CH_4$ (27 %) than for $^{14}CO_2$ (5

533 %). Another source of aged CH_4 could be deep peat derived CH_4, as suggested by Garnett et al. (2012c). While

534 measured porewater CH_4 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_4. 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 ^{14}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 $\delta^{13}CH_4$ signatures between the peatland and riparian areas indicate not

547   only the varying carbon dynamics involved in the production of CO_2 and CH_4 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_2 or CH_4. 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_2 and CH_4 but with a component from geogenic sources of up to 5 % for CO_2 and 28 % for CH_4. This

556   suggests that the stream bed may be acting as a pathway by which carbonate weathering derived CO_2 and deep

557   geologically derived coal bed CH_4 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_2 and 28 % for CH_4. 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.

577 Acknowledgements

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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 Ls^{-1}). Values are calculated for
910 April and September sampling periods and for the whole of 2012

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

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Table 2 Soil properties for the horizons shown in Figure 3. No samples were collected from the riparian C1
horizon and the peatland O1 horizon as they were too thin for sample collection

Soil	Horizon	Bulk density (g cm^{-3})	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** αC values for the soil gases. [a] indicates CO_2 reduction and [b] acetate fermentation as the likely
959 production pathway based on Whiticar et al. (1986).
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Site	Sample type	April αC	September αC
Peatland	Soil (40-45cm)	1.072[a]	1.071[a]
	Soil (40-45cm)	1.075[a]	1.060[a]
	Soil (40-45cm)	1.072[a]	1.066[a]
	Soil (65-70) cm	1.075[a]	1.074[a]
	Soil (40-45cm)	/	1.047[b]
Riparian Zone	Soil (40-45cm)	1.073[a]	1.061[a]
	Soil (40-45cm)	1.078[a]	1.046[b]
	Soil (65-70) cm	1.066[a]	1.056[a]

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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}C analysis so small sample AMS used with δ^{13}C determined online by the AMS
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Sample	Publication Code (SUERC-)	^{14}C Enrichment (%modern ± 1 σ)	Radiocarbon age (years BP ± 1 σ)	δ^{13}C (± 0.1 ‰)
Soil				
Peat (5-10 cm)	40585	98.34 ± 0.45	134 ± 37	-27.9
Peat (25-30 cm)	44328	88.88 ± 0.45	947 ± 41	-26.7
Peat (45-50 cm)	40586	94.45 ± 0.43	459 ± 37	-27.4
Peat (65-70 cm)	44329	93.36 ± 0.41	552 ± 35	-29.9
Peat (145-150 cm)	40587	92.05 ± 0.42	665 ± 37	-28.5
Riparian (5-10 cm)	40588	87.13 ± 0.40	1107 ± 37	-27.0
Riparian (25-30 cm)	44330	90.98 ± 0.42	759 ± 37	-27.6
Riparian (45-50 cm	40589	89.03 ± 0.41	933 ± 37	-27.8
Riparian (65-70 cm)	44331	83.93 ± 0.37	1407 ± 36	-27.6
Riparian (75-80 cm)	40590	87.53 ± 0.40	1070 ± 37	-28.0
Soil CO_2				
Apr - SPa - CO_2	40571	103.40 ± 0.47	Modern	-12.0
Apr - SPb -CO_2	40575	104.19 ± 0.48	Modern	-12.0
Apr - SPc - CO_2	40577	103.39 ± 0.47	Modern	-11.0
Apr - DP - CO_2	44297	102.90 ± 0.48	Modern	-7.8
Apr - SRb - CO_2	40578	103.36 ± 0.47	Modern	-19.8
Apr - SRc - CO_2	40579	105.66 ± 0.45	Modern	-21.0
Apr - DR - CO_2	44298	101.22 ± 0.45	Modern	-15.2
Sept - SPa-CO_2	44299	105.02 ± 0.49	Modern	-11.0
Sept - SPb-CO_2	44300	103.65 ± 0.48	Modern	-17.4
Sept - SPc-CO_2	44301	105.07 ± 0.49	Modern	-10.7
Sept - DP-CO_2	44304	102.58 ± 0.45	Modern	-6.9
Sept - SRa-CO_2	44305	103.36 ± 0.48	Modern	-16.0
Sept - SRb-CO_2	44306	101.50 ± 0.51	Modern	-14.3
Sept - SRc-CO_2	44307	104.67 ± 0.49	Modern	-17.1
Sept - DR-CO_2	44308	100.73 ± 0.47	Modern	-13.2
Soil CH_4				
Apr - SPa – CH_4	40570	104.51 ± 0.48	Modern	-78.4
Apr - SPb –CH_4	40572	104.25 ± 0.45	Modern	-81.3
Apr - SPc - CH_4	40576	104.41 ± 0.45	Modern	-77.5
Apr - DP - CH_4	44296	102.73 ± 0.48	Modern	-77.2
Apr - SRb - CH_4	40492*	102.40 ± 0.51	Modern	-86.6
Apr - SRc - CH_4	40505*	104.56 ± 0.53	Modern	-92.1
Apr - DR - CH_4	46329*	99.00 ± 0.94	81 ± 77	-76.0
Sept - SPa- CH_4	43509	105.46 ± 0.49	Modern	-76.9
Sept - SPb- CH_4	46330*	104.78 ± 1.01	Modern	-73.0
Sept - SPc- CH_4	43510	105.26 ± 0.47	Modern	-71.8
Sept - DP- CH_4	43511	103.16 ± 0.48	Modern	-75.1
Sept - SRa- CH_4	43514	103.04 ± 0.48	Modern	-60.5
Sept - SRb- CH_4	46331*	103.71 ± 1.44	Modern	-70.7
Sept - SRc- CH_4	43515	104.89 ± 0.46	Modern	-60.7
Sept - DR- CH_4	43516	102.07 ± 0.48	Modern	-65.9
Chamber CO_2				
Apr - Peatland- CO_2	43494	104.79 ± 0.49	Modern	-25.9
Apr - Riparian -CO_2	43496	100.55 ± 0.47	Modern	-26.6
Apr - Evasion - CO_2	43490	98.86 ± 0.46	36 ± 37	-17.4
Sept - Peatland- CO_2	43500	105.70 ± 0.49	Modern	-26.3
Sept - Riparian -CO_2	43504	100.99 ± 0.47	Modern	-27.1

Sept - Evasion - CO$_2$	43498	101.39 ± 0.45	Modern	-20.5
Chamber CH$_4$				
Apr - Peatland- CH$_4$	43491	107.29 ± 0.48	Modern	-63.2
Apr - Riparian - CH$_4$	43495	101.79 ± 0.48	Modern	-75.9
Apr - Evasion - CH$_4$	43489	93.19 ± 0.44	537 ± 38	-58.1
Sept - Peatland- CH$_4$	43499	108.25 ± 0.50	Modern	-58.0
Sept - Riparian - CH$_4$	43501	104.84 ± 0.49	Modern	-63.5
Sept - Evasion - CH$_4$	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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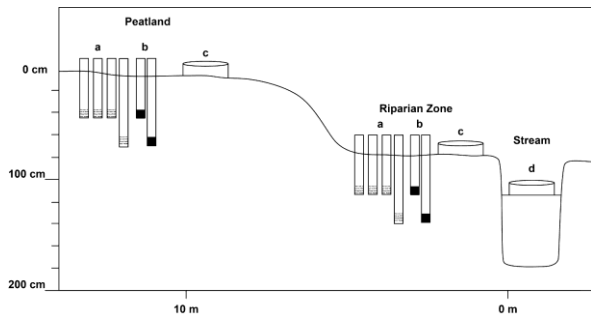
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1010 **Fig. 1** Schematic of the transect setup used in this study. Sampling probes installed at 40 cm and 70 cm depth
1011 for the collection of (a) soil gases (CO_2 and CH_4) and (b) soil DOC in both the peatland and riparian zone.
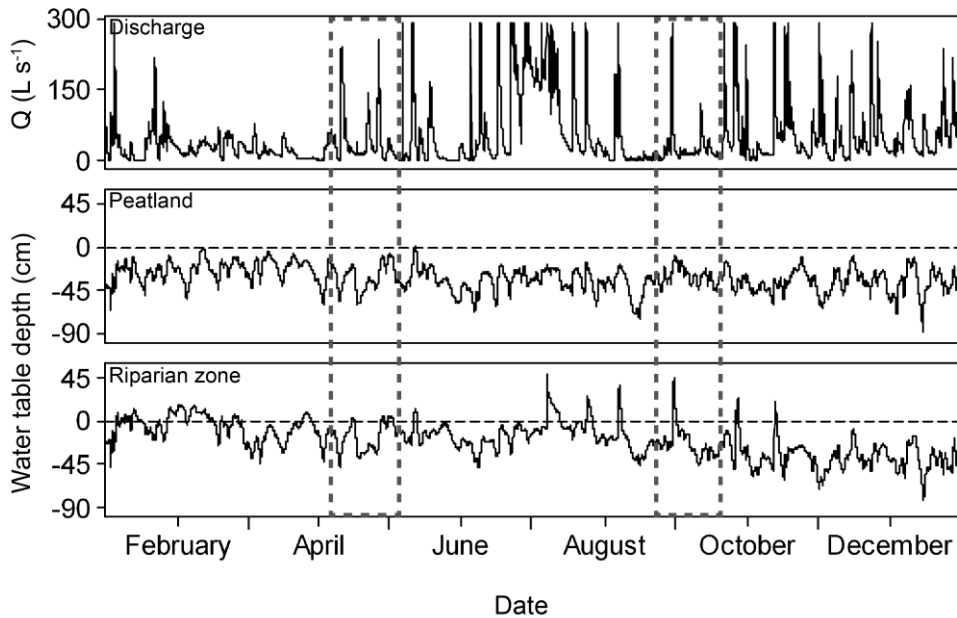1012 Chambers (c) and (d) represent static chambers for the collection of soil emission CO_2 and CH_4, and a floating
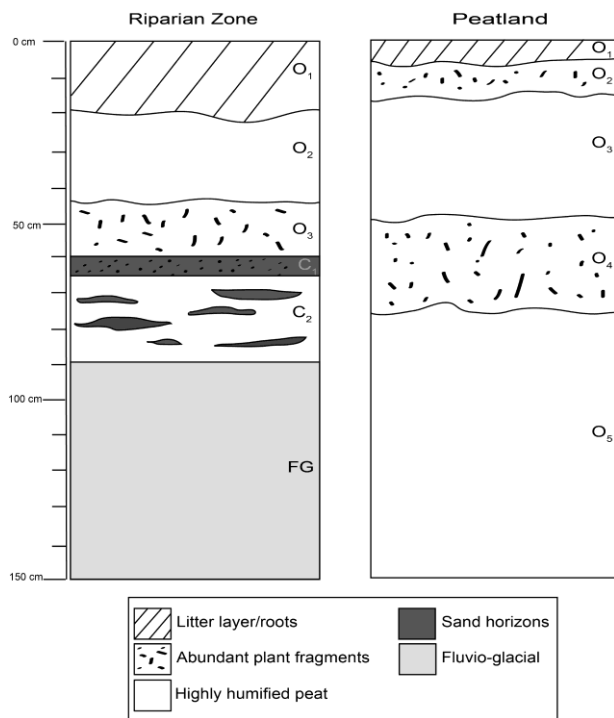1013 chamber for the collection of evasion CO_2 and CH_4, respectively

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1016 **Fig. 2** Graphs showing a) Discharge (Q), b) water table position in the peatland and c) water table position in the
1017 riparian zone across the full year 2012. The April and September isotope sampling periods are highlighted by
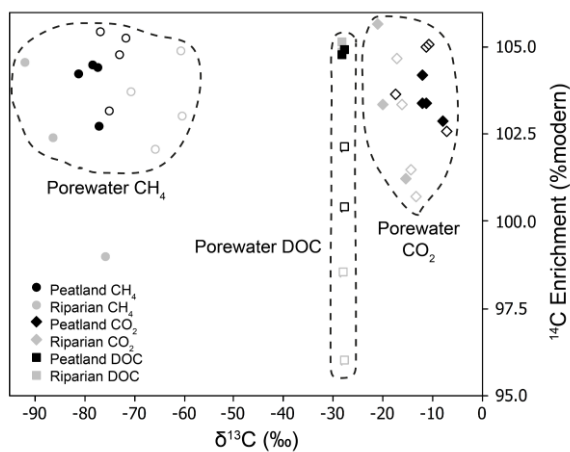1018 dashed boxes

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1020 **Fig. 3** Soil profiles from 0 to 150 cm for the riparian zone and the peatland. O1, O2, O3, O4 and O5 represent
1021 organic soil horizons, C1 and C2 represent organo-mineral horizons and FG represents the underlying fluvio-
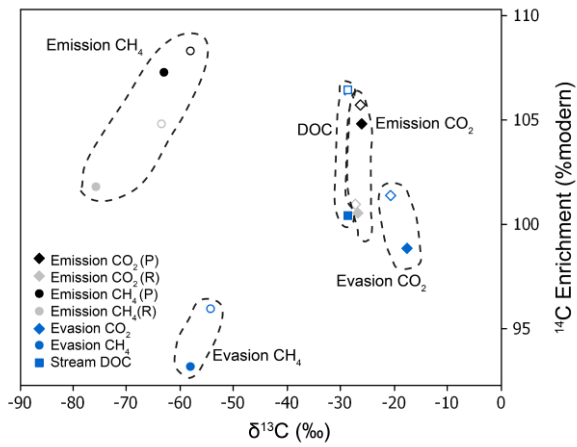1022 glacial horizon
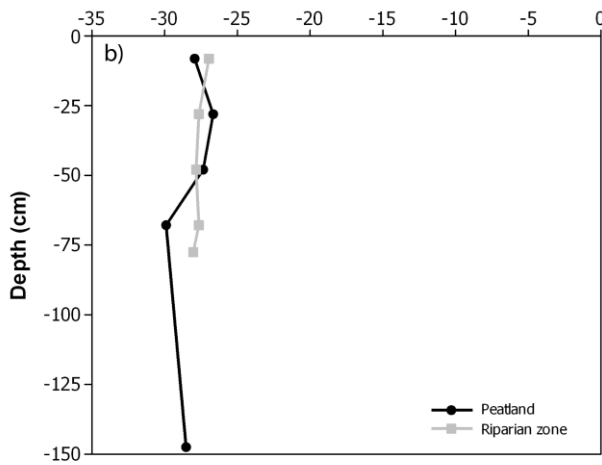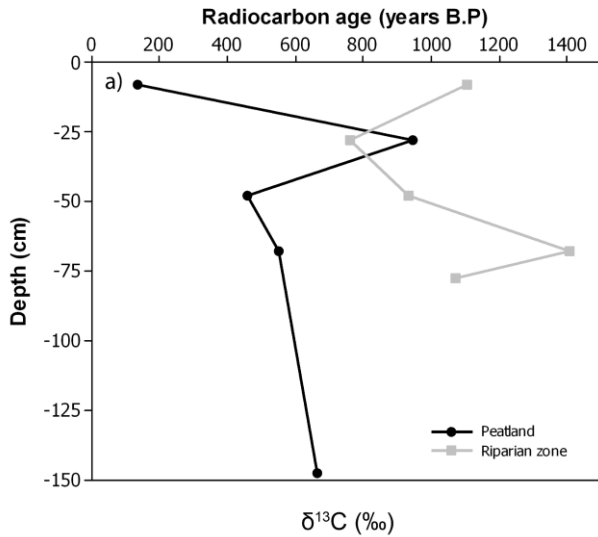
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1024   **Fig. 4** Soil profiles of a) radiocarbon age (years BP) and b) $\delta^{13}C$ (‰) in the peatland and riparian zone

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1027   **Fig. 5** ^{14}C / $\delta^{13}C$ scatterplot of porewater CO_2, 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]C / δ^{13}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
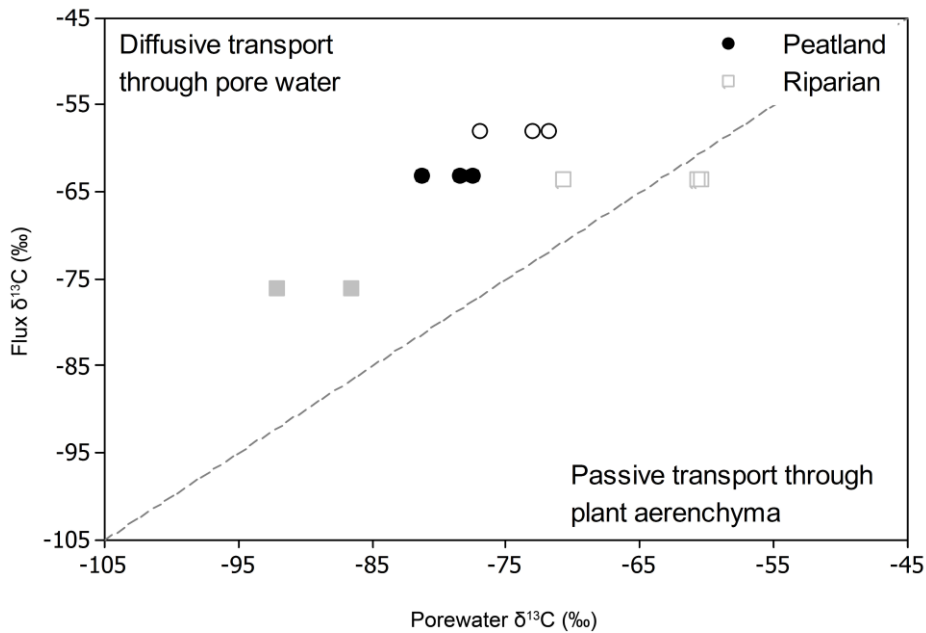
1033

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