

1 **Should aquatic CO₂ evasion be included in contemporary carbon budgets for**
2 **peatland ecosystems?**

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11
12 **Abstract**

13 Quantifying the sink strength of northern hemisphere peatlands requires
14 measurements or realistic estimates of all major C flux terms. Whilst assessments of
15 the net ecosystem carbon balance (NECB) routinely include annual measurements of
16 net ecosystem exchange and lateral fluxes of dissolved organic carbon (DOC), they
17 rarely include estimates of evasion (degassing) of CO₂ and CH₄ from the water
18 surface to the atmosphere, despite supersaturation being a consistent feature of
19 peatland streams. Instantaneous gas exchange measurements from temperate UK
20 peatland streams suggest that the CO₂ evasion fluxes scaled to the whole catchment
21 are a significant component of the aquatic C flux (23.3 ± 6.9 g C m⁻² catchment yr⁻¹)
22 and comparable in magnitude to the downstream DOC flux (29.1 ± 12.9 g C m⁻²
23 catchment yr⁻¹). Inclusion of the evasion flux term in the NECB would be justified if
24 evaded CO₂ and CH₄ were isotopically “young” and derived from a “within-
25 ecosystem” source, such as peat or in-stream processing of DOC. Derivation from

1 “old” biogenic or geogenic sources would indicate a separate origin and age of C
2 fixation, disconnected from the ecosystem accumulation rate that the NECB definition
3 implies. Dual isotope analysis ($\delta^{13}\text{C}$ and ^{14}C) of evasion CO_2 and DOC strongly
4 suggest that the source and age of both are different and that evasion CO_2 is largely
5 derived from allochthonous (non-stream) sources. Whilst evasion is an important flux
6 term relative to the other components of the NECB, isotopic data suggest that its
7 source and age are peatland-specific. Evidence suggests that a component of the CO_2 -
8 C evading from stream surfaces was originally fixed from the atmosphere at a
9 significantly earlier time (pre-AD1955) than modern (post-AD1955) C fixation by
10 photosynthesis.

11

12 **1. Introduction**

13 Northern hemisphere peatlands are a huge global repository of organic C (estimates
14 vary between 200-450 Pg C (Gorham 1991; Turunen and others 2002)) and its
15 breakdown products. The latter are released directly as CO_2 , CH_4 and dissolved and
16 particulate organic carbon (DOC and POC) into freshwater systems from which direct
17 gaseous losses of C (evasion or degassing) to the atmosphere occurs. The magnitude
18 of the aquatic C loss pathway is of significant interest, particularly as the climate
19 warms and sink-source relationships of peatlands change (IPCC, 2007). Where the
20 evasion flux has been quantified (Kling and others 1991; Dinsmore and others 2010)
21 data have shown that it is a significant component of the NECB and on a catchment-
22 scale is of the same order of magnitude as the lateral flux of DOC (Hope and others
23 2001; Wallin and others 2013). The NECB, defined as the net rate of carbon
24 accumulation or loss from an ecosystem, includes two flux terms that are directly
25 linked to the aquatic pathway, net dissolved inorganic and organic C inputs/losses

1 (F_{DIC} and F_{DOC}) (Chapin and others 2006). The conceptual framework of the NECB
2 also explicitly defines its lower physical limits, which in the case of terrestrial
3 ecosystems is below the rooting zone, and for freshwater ecosystems the bottom of
4 either the sediments or the water column (Chapin and others 2006). Changes in both
5 the annual C balance and NECB are now being routinely measured across northern
6 hemisphere peatlands in order to quantify changes in C sink strength. Measurement
7 periods range from 2-6 years and include studies from Scotland (1996-98, 2007-08),
8 Canada (1998-2004), Sweden (2004-05) and Ireland (2003-08) (Billett and others
9 2004; Dinsmore and others 2010; Roulet and others 2007; Nilsson and others 2008;
10 Koehler and others 2011).

11 The fact that streams and rivers associated with peatland systems are
12 consistently supersaturated with respect to CO_2 and CH_4 (Hope and others 2001;
13 Dinsmore and Billett 2008; Wallin and others 2011) is a clear indication of the
14 degassing potential of the aquatic system. Both gases are lost from the aquatic
15 pathway as surface water gas concentrations progressively equilibrate with lower
16 concentrations in the atmosphere. This has been demonstrated in downstream spatial
17 measurements of pCO_2 and pCH_4 in which high concentrations are directly related to
18 the spatial distribution of peat soils (Dawson and others 2002; Billett and Moore
19 2008) and where outgassing occurs in the proximity of source areas (Nilsson and
20 others 2008). Measurements from the UK, N America and Sweden show that
21 significant amounts of gas exchange occur across the water-air interface of peatland
22 streams (Billett and Moore 2008; Billett and Harvey 2013; Wallin and others 2011).
23 However, a lack of water-air flux measurements in small headwater streams has often
24 led to the use of estimated or modelled values of gas transfer coefficients or velocities
25 in regional upscaling (e.g. Teodoru and others 2009). Accurate flux estimates are also

1 hindered by poor quantification of water surface area in low order streams. Hence
2 there is still much uncertainty about the magnitude of the CO₂ evasion flux and its
3 origin. This uncertainty has been recently improved by studies that show that K_{CO_2}
4 (the gas transfer coefficient of CO₂) can be predicted by a combination of slope and
5 stream width/depth (Wallin and others 2011) or slope and stream velocity (Butman
6 and Raymond 2011). In addition, the ability to measure CO₂ concentrations at higher
7 temporal resolution has greatly improved understanding of aquatic CO₂ hydro-
8 dynamics (Johnson and others 2010, Dinsmore and others 2013).

9 Whilst flux terms and the methods used to measure C exchange are well
10 established for land-atmosphere gas exchange and downstream aquatic losses, evasion
11 (degassing of CO₂ and CH₄ at the water surface) is less well understood and often
12 poorly quantified or even worse, ignored. Most eddy covariance measurement
13 systems exclude standing or flowing water and leave the evasion flux unmeasured
14 (e.g. Billett and others 2004). Hence in a continental or global context the magnitude
15 of the evasion flux is a major “unknown” (Cole and others 2007), although estimates
16 for US streams and rivers suggest they release 97 ± 32 Tg of C to the atmosphere each
17 year (Butman and Raymond 2011). Globally it has been estimated that CO₂ evasion
18 from inland waters is of similar magnitude to CO₂ uptake by the oceans (Tranvik and
19 others 2009). In arctic lakes and streams it represents 25-50% of the net annual
20 landscape carbon accumulation rate (Kling and others 1991). In the whole Yukon
21 catchment (854,700 km²) Striegl and others (2012) have estimated that gas emissions
22 from the water surface account for 50% of the total lateral C export. Collectively these
23 values suggest that the evasion flux represents an important loss of carbon and GHGs
24 (greenhouse gases) from peatland ecosystems that include the aquatic pathway.
25 Because the overall concept of the NECB is to assess the net rate of ecosystem C

1 accumulation (“sink strength”), the inclusion of evasion CO₂ in NECB calculations
2 will be justified if it is derived wholly from (1) lateral transport to the stream of
3 “young” soil-derived CO₂, (2) within-stream decomposition of DOC and POC or (3)
4 C fixed by within-stream photosynthesis. However, if CO₂ lost by evasion to the
5 atmosphere is “old” and originates from outside the ecosystem boundary (for
6 example, from a geogenic source or below the active rooting zone), inclusion in the
7 NECB would not be justified and lead to an under-estimation of the current sink
8 strength of peatland systems. Whilst “young and old” carbon could be defined in
9 several ways, a chronological tool is required to provide an unambiguous definition.
10 Here we measure the relative age of C based on its radiocarbon concentration (Levin
11 and Hesshaimer 2000); “young” C is defined as C fixed from the atmosphere post-
12 AD1955 that is ¹⁴C enriched (>100% modern) due to nuclear weapons testing (post-
13 bomb); “old” or pre-bomb C is ¹⁴C depleted and was fixed pre-AD1955. In addition,
14 if the source of the CO₂ lost by evasion is both allochthonous and constitutes old
15 stored carbon rather than young recently fixed/respired terrestrial carbon,
16 contemporary NECB estimates would be influenced by carbon fixed during a different
17 era. The concept of an NECB to assess carbon accumulation in terrestrial ecosystems
18 is only useful when the timescales of C fixation are comparable and allow for
19 interaction between individual components; hence it is important that non-
20 contemporary C (for example derived from geological sources or peat produced more
21 than 60 years ago) be excluded.

22 Here we aim to address the issue of inclusion of aquatic C in the NECB by
23 firstly assessing the magnitude of the fluxes by comparing instantaneous
24 measurements of CO₂ evasion and DOC fluxes from 6 UK peatland sites, and then
25 producing estimates of catchment scale evasion fluxes using measurements of water

1 surface area. We then uniquely combine C flux and dual isotope $\delta^{13}\text{C}$ and ^{14}C
2 measurements from the same sites to answer the following questions; (1) is C evaded
3 as CO_2 allochthonous (defined as aquatic C derived from terrestrial sources), or is it
4 autochthonous (defined as aquatic C produced by in-stream C fixation), and (2)
5 should evasion CO_2 be considered as part of the contemporary NECB of peatlands
6 (we define contemporary in this case as our measurement period 2004-2008), or is it
7 derived from an older (pre-AD1955) C pool?

8

9 **2. Sites and Methods**

10 Between 2004-2006 instantaneous aquatic C flux measurements were carried out in
11 peatlands in Scotland (Loch More; Auchencorth Moss), northern England (Moor
12 House; Bleaklow) and Wales (Migneint; Plynlimon). Catchment characteristics are
13 summarised in Table 1. Seven 1st to 3rd order streams in total were studied, the
14 Achscoriclate Burn (Loch More), Black Burn (Auchencorth Moss), Cottage Hill Sike
15 (CHS) and Rough Sike (both Moor House), Doctor's Gate Clough (Bleaklow), Afon
16 Ddu (Migneint) and Afon Hafren (Plynlimon). The host catchments vary in altitude
17 and size from 121-746 m and 0.2-4.7 km², respectively with mean annual
18 precipitation ranging from 1129 mm (Loch More, the most northerly site) to 2746 mm
19 (Plynlimon, the most westerly site). Mean annual air temperature ranged from 5.3-
20 10.0°C. Peatland catchments are typically semi-natural and affected to varying
21 degrees by low levels of (often seasonal) grazing and in some cases drainage.
22 Hydrologically the streams are typically “flashy” with a rapid rainfall-runoff response
23 and a wide range in discharge values (Table 1). Streamwater chemistry is
24 characterised by low pH, low Ca and high DOC concentrations (Billett et al. 2007).
25 For further details of the 7 streams refer to Billett and Harvey (2013).

1 Between 2-10 concurrent instantaneous flux measurements of vertical CO₂ (and
 2 CH₄) evasion and lateral aquatic C (DOC, DIC, CO₂ and CH₄) were made at each of 2
 3 locations at the 6 peatland sites (12 sites in total). The evasion flux was measured using
 4 a combination of gas (propane) and soluble tracer injection along 18-23 m long reach
 5 lengths. The calculated (K_{CO_2} or K_{CH_4}) gas transfer coefficient was converted to an
 6 instantaneous CO₂ or CH₄ evasion flux using the following equation:

7 Instantaneous evasion flux ($\text{mg C m}^{-2} \text{ s}^{-1}$) = $\frac{\Delta_{CO_2} (\Delta_{CH_4}) \times K_{CO_2} (K_{CH_4}) \times \tau \times Q}{R}$
 8
 9

10 where Δ_{CO_2} or Δ_{CH_4} is the difference in the dissolved gas concentrations in the study
 11 reach if the stream was at atmospheric equilibrium (mg C L^{-1}), K_{CO_2} or K_{CH_4} is the gas
 12 transfer coefficient (min^{-1}), τ is the reach length travel time (min), Q is the average
 13 reach discharge (L s^{-1}) measured on each occasion at both ends of the study reaches
 14 using either a continuous or pulse injection of NaCl tracer, and R the water surface area
 15 of the reach (m^2). Full details of the methodology and flux calculations are given in
 16 Billett and Harvey (2013).

17 Dissolved CO₂ and CH₄ were measured directly at both ends of the study reach
 18 using headspace analysis (Kling and others 1991; Hope and others 1995; Hope and
 19 others 2001). This technique requires measurement of ambient atmospheric CO₂/CH₄
 20 concentration, stream temperature, atmospheric pressure and elevation above mean sea
 21 level. A HP5890 Series II with Flame Ionisation Detector (FID) and attached
 22 methaniser was used to determine CO₂ and CH₄ concentrations (CO₂ and CH₄ detection
 23 limits 10 ppmv and 70 ppbv, respectively). Two filtered (0.45 μm PTFE) water samples
 24 (60 ml) were collected for the determination of DOC concentration. After sample
 25 acidification and sparging with N₂, DOC concentration was determined by digestion/uv
 26 oxidation using a Rosemount Dohrman DC-80 TOC Analyser (detection limit 0.1 mg L^{-1}
 27 ¹; precision $\pm 0.04 \text{ mg L}^{-1}$). DIC concentration was calculated from the difference

1 between the concentration of total dissolved carbon (DOC+DIC) in an unacidified
2 sample and DOC concentration.

3 Instantaneous CO₂ and CH₄ (vertical) evasion fluxes (mg C m⁻² s⁻¹) were
4 compared to the lateral (downstream) flux of various C species (DOC, DIC, CO₂ and
5 CH₄) by expressing all flux rates per unit area of catchment (mg C ha⁻¹ catchment s⁻¹).
6 Downstream fluxes were calculated by multiplying concentration (µg or mg C L⁻¹) by
7 flow (L s⁻¹) and dividing by the catchment area upstream of the sample point. For
8 evasion we make the simplifying assumption that the measured evasion rate was
9 representative of the upstream channel area. Although we made evasion measurements
10 along 2 representative reaches in the middle and lower sections of each stream, we
11 know that evasion rate has high spatial variability (see Billett & Harvey 2013 for
12 individual measurements). Then we calculated the water surface area in each catchment
13 from the active drainage area length (including all flowing tributaries) and the average
14 width of all the streams/tributaries within the drainage system. The former was
15 calculated from detailed base maps and ground truthing, the latter by multiple
16 measurements (10 m spacing) of stream width in the field. Catchment-scale evasion
17 rates (allowing comparison with downstream C fluxes) were calculated as follows:

18 CO₂ or CH₄ evasion flux (mg C ha⁻¹ catchment s⁻¹) =
19
$$\frac{\text{Instantaneous flux (mg C m}^{-2} \text{ s}^{-1}) \times \text{catchment water surface area (ha)}}{\text{upstream catchment area (ha)}}$$

20

21 Simultaneous measurements of the δ¹³C and ¹⁴C content of evasion CO₂-C and DOC-
22 C were carried out on several of the UK peatland streams as well as 2 headwater
23 streams in Finnish peatlands. Sufficient evasion CO₂ for ¹⁴C analysis by accelerator
24 mass spectrometry (AMS) was collected directly in the field using a molecular sieve
25 linked to a floating chamber. The ¹⁴C content of DOC was determined from 1L water
26 samples that were subsequently filtered and freeze dried. For further details of the

1 methodology see Billett and others 2007; Billett and others 2012a; Billett and others
2 2012b).

3

4 **3. Results and Discussion**

5 Mean streamwater concentrations (mg C L^{-1}) of C species (Table 2) were dominated
6 by DOC (14.1) with lower amounts of DIC (3.8), CO_2 (1.4) and CH_4 (0.01).
7 Dissolved gas concentrations are equivalent to mean $ep\text{CO}_2$ and $ep\text{CH}_4$ values of 6.1
8 and 193, respectively (excess partial pressure or ep is the concentration of the
9 dissolved gas in the water sample divided by its concentration in pure water at
10 atmospheric equilibrium, Neal and others 1998). Discharge rates at the times the flux
11 measurements were made were $0.8\text{-}374.4 \text{ L s}^{-1}$ (mean 45.1). Mean % water surface
12 area within all the headwater catchments was 0.20% ($n=7$, range 0.07-0.37%). This is
13 one of the most important steps involved in upscaling reach-scale to catchment-scale
14 evasion fluxes. Our measured average value compares favourably with mean
15 estimates of 0.14% from a large number of boreal peatland streams (mean catchment
16 area 67 km^2) in NW Québec (Teodoru and others 2009) and 0.19% from 1st to 4th
17 order headwater streams ($n=13$) in boreal Sweden (Wallin and others 2011). In
18 addition, Hope and others (2001) estimated stream water surface area as 0.22% from a
19 small (1.3 km^2) headwater peatland catchment in NE Scotland. At a much larger
20 scale, Butman and Raymond (2011) used a higher value of 0.52% (regional range
21 0.23-0.84%) for the stream/river water surface area between 25°N and 50°N in the
22 USA; this value however included stream orders 1 to 10.

23 Both catchment scale CO_2 evasion and DOC fluxes were similar and
24 significantly related to flow, although the relationship between discharge and DOC
25 flux was strongest (Fig. 1). Our catchment-scale evasion rates are likely to under-

1 estimate the size of the overall flux because, whilst they include hydrological
2 variability, they only include a small degree of spatial variability and exclude the
3 source areas that are often associated with high $p\text{CO}_2$ and $p\text{CH}_4$ (e.g. Nilsson and
4 others 2008). If the data from all sites are considered collectively the CO_2 evasion flux
5 ($7.38 \pm 15.34 \text{ mg C ha}^{-1} \text{ catchment s}^{-1}$) was equivalent to the downstream export of
6 DOC ($9.24 \pm 28.56 \text{ mg C ha}^{-1} \text{ catchment s}^{-1}$) and 10x larger than the downstream
7 (lateral) export of $\text{CO}_2\text{-C}$ (Table 2). Overall median $\text{CO}_2\text{-C}$ evasion fluxes were higher
8 than the median DOC fluxes at the sites. Fluxes of CH_4 (either as evasion or
9 downstream export) were more than 2 orders of magnitude lower than the equivalent
10 CO_2 flux.

11 The values presented in Fig. 1 can be used to make a first approximation of
12 fluxes from each individual catchment (Table 3), although the small number of
13 measurements for each catchment means that individual values have to be treated with
14 a degree of caution. Despite this caveat, annual upscaled CO_2 evasion fluxes for
15 individual catchments were mostly in the range $9\text{-}27 \text{ g C m}^{-2} \text{ catchment yr}^{-1}$ and DOC
16 fluxes in the range $2\text{-}29 \text{ g C m}^{-2} \text{ catchment yr}^{-1}$; only the Hafren catchment showed a
17 significant difference between flux values. We derive overall annual CO_2 evasion and
18 DOC flux values from all our peatland headwater streams of 23.3 ± 6.9 and 29.1 ± 12.9
19 $\text{g C m}^{-2} \text{ catchment yr}^{-1}$, respectively (Table 3). We compared these values to
20 published DOC fluxes from 6 of the sites derived from long-term datasets (2 to 16 yr)
21 based on a weekly or 2 weekly sampling frequency (Table 2). Both our overall CO_2
22 evasion and DOC fluxes were comparable to the long-term published DOC flux value
23 ($25.0 \text{ g C m}^{-2} \text{ catchment yr}^{-1}$) derived from all the sites (Table 3). We are therefore
24 confident that the overall flux values derived from a relatively small number of

1 individual measurements in the 7 catchments, were representative of the peatland
2 system in terms of its inherent variability associated with discharge and season.

3 Whilst several recent studies (e.g. Wallin and others 2013) have also
4 demonstrated the similarity in catchment-scale CO₂ evasion and DOC fluxes from
5 peatland headwater streams and therefore highlight the importance of the aquatic
6 pathway as a significant catchment carbon loss, relatively little is known about the
7 source of the evaded CO₂ and whether it should be included in calculations of the
8 contemporaneous NECB. We carried out concurrent dual isotope measurements ($\delta^{13}\text{C}$
9 and ^{14}C) of both evasion CO₂-C and DOC-C at 4 of the temperate UK peatland sites
10 described above (Billett and others 2007; Billett and others 2012a) as well as in 2
11 boreal forested peatland headwater streams in N Karelia, Finland (Billett and others
12 2012b). Here for the first time we bring the isotope (Fig. 2, Table 4) and flux data
13 together and use it to compare the age and source of both C species. The evasion
14 isotope values have been corrected to account for CO₂ degassing into a closed
15 collection chamber (Billett and Garnett 2010).

16 Evasion CO₂ was consistently and significantly more ^{13}C enriched than DOC
17 in all 5 peatland catchments, with only 3 pairs of samples (total = 52) exhibiting
18 similar $\delta^{13}\text{C}$ values (-27.6 to -28.4 ‰). Individual catchments were characterised by a
19 specific range in $\delta^{13}\text{C}$ -CO₂, with the Finnish sites being the most ^{13}C depleted and the
20 Loch More (UK) sites the most ^{13}C enriched. The source, or more likely sources, of
21 evasion CO₂ are therefore different from DOC, with the former derived either from
22 decomposition of C3 plant material ($\delta^{13}\text{C} \approx -28$ ‰), atmospheric CO₂ ($\delta^{13}\text{C} \approx -8$ ‰),
23 geological weathering ($\delta^{13}\text{C} \approx 0$ ‰) or CO₂ resulting from anaerobic fermentation
24 ($\delta^{13}\text{C} \approx -14$ to $+10$ ‰) (Billett and others 2007; Billett and others 2012a). Compared

1 to CO₂, δ¹³C-DOC values varied little and were consistent with a single source,
2 namely decomposition of organic matter derived from C3 plants.

3 At all sites DOC was consistently and significantly more ¹⁴C enriched than
4 evasion CO₂ with individual catchments characterised by a distinct clustering of
5 values (Fig. 2). With one exception (Auchencorth Moss), the radiocarbon content of
6 DOC samples was young and close to the contemporary atmospheric value (107-105
7 % modern, estimated from Levin and others 2008) for the time of sampling (2004-
8 2008). These observations indicate that the DOC contained a substantial component
9 of post-bomb C (i.e. carbon originally fixed after AD1955). The most ¹⁴C enriched
10 CO₂ samples were from N Karelia, Finland (mean 107.69±1.94 % modern), which
11 again indicated that this CO₂ was radiogenically young and substantially derived from
12 carbon fixed during the post-bomb era. In contrast, CO₂ from most UK sites had ¹⁴C
13 concentrations <100 %modern, reflecting a component of old pre-bomb carbon (i.e.
14 carbon fixed before ~AD1955); the most ¹⁴C depleted (i.e. oldest) CO₂ was from Loch
15 More (aged up to 1502±28 years BP) and Auchencorth Moss (aged up to 1163±29
16 years BP). However, all sites did at times provide CO₂ samples with ¹⁴C
17 concentrations >100 %modern, indicating younger post-bomb carbon.

18 The difference in the δ¹³C and ¹⁴C signatures of DOC and evasion CO₂
19 strongly suggest that a significant proportion of CO₂ lost by evasion is not derived
20 from within-stream breakdown of DOC. A non-stream source in peatland systems is
21 also supported by published non-isotopic data showing a strong link between temporal
22 changes in soil atmosphere and stream CO₂ concentrations (Hope and others 2004;
23 Dinsmore and Billett 2008). In addition, the isotopic signature of CO₂ evasion at most
24 of the sites appears to have either a deeper biogenic (peat) or a geogenic (weathering)
25 component and thus originates from outside the physical lower ecosystem boundary

1 associated with the strict definition of the NECB (Chapin and others 2006). The
2 timescales of geogenic CO₂ production versus contemporary carbon cycling also leads
3 to challenges in interpreting the NECB, suggesting inclusion of this evaded CO₂
4 component may not be appropriate. There are peatland sites (e.g. Loch More and
5 Auchencorth Moss) where the source and age of CO₂ and DOC are significantly
6 different (Fig. 2) whilst there are others, such as the forested Finnish peatland sites,
7 where the isotopic signatures are much closer and more characteristic of DOC and
8 CO₂ produced from recently fixed C (Billett and others 2012b). Hence, whilst the
9 isotopic data can be explained by a mixture of sources in most of these acidic low
10 productivity systems, CO₂ evasion is likely to be primarily derived from non-stream
11 sources. A similar conclusion was reached in the Yukon River and its tributaries,
12 where Wickland and others (2012) found that biodegradation of soil-derived DOC
13 only accounted for <6% of the total CO₂ emission from the water surface.

14 Compared to DOC, the source of evasion CO₂ varies significantly from
15 peatland to peatland and we present evidence to show that old (pre-AD1955) CO₂ is
16 being released into the atmosphere from a number of sites. This is significant because
17 it suggests that the contemporary C balance of peatlands is being affected by the
18 release of C from an older (pre-AD1955) and deeper (primarily sub-rooting zone) C
19 pool, the contribution of which varies spatially between peatlands. Whilst DOC at
20 these sites can almost exclusively be regarded as the result of turnover of young
21 organic C, evasion CO₂ cannot be regarded solely as the breakdown product of
22 recently fixed and respired terrestrial carbon. At the UK peatland sites there is strong
23 evidence to suggest that the evaded CO₂ is derived from multiple sources including
24 decomposition of deep peat (biogenic) and carbonate weathering (geogenic) (Billett
25 and others 2007; Billett and others 2012a). We have recently shown that the age of

1 aquatic dissolved CO₂ at the Auchencorth Moss catchment varied from 707 to 1210
2 years BP during a single hydrological year (Garnett and others 2012), with the oldest
3 and youngest CO₂ associated with low (deep source) and high discharge (shallow
4 source), respectively. Because the δ¹³C-CO₂ values were relatively constant (-23.0 to -
5 24.2 ‰) the isotope data indicates that the CO₂ is predominantly derived from a single
6 biogenic peat source that varies in depth during the hydrological year. The release of
7 CO₂ of variable age and source from natural peatland pipes to the atmosphere (Billett
8 and others 2012a) further supports the potential for the involvement of a deeper, old C
9 pool in measurements of the contemporary C balance, originating from outside the
10 ecosystem boundaries normally associated with the NECB.

11

12 **4. Conclusions**

13 Our best current estimate for the size of the evasion flux term from UK peatland
14 headwater streams is 23.3 g C m⁻² catchment yr⁻¹, which is of similar magnitude to the
15 UK lateral DOC flux estimate of 19-27 g C m⁻² catchment yr⁻¹ for the same type of
16 stream system (Billett and others 2010). Upscaled to a national level using a value of
17 24,640 km² for the UK peatland area (Billett and others 2010), we estimate that the
18 CO₂ evasion flux from peatland streams represents an additional natural emission
19 source of the order of 0.57 Mt C yr⁻¹ to the atmosphere. Given the errors associated
20 with the evasion estimate (Table 3) and the area of UK peatlands (values range from
21 17,500 km² to 32,830 km²; Joosten & Clark 2002, JNCC 2011), the UK peatland CO₂
22 evasion emission value could range from 0.29-0.99 Mt C yr⁻¹. To put this into context
23 Hope and others (1997) and Worrall and others (2012) have independently estimated
24 a total DOC loss from British rivers to tidal waters of 0.68±0.07 Mt C yr⁻¹ and
25 0.91±0.35 Mt C yr⁻¹, respectively. The value of 0.57 Mt C yr⁻¹ is higher than that

1 estimated for the loss of C from the drainage of UK fenlands (0.5 Mt C yr^{-1}) and from
2 peat extraction (0.2 Mt C yr^{-1}) (Cannell and others 1999).

3 We combined instantaneous flux measurements of DOC and CO_2 evasion with
4 isotopic evidence to demonstrate both the magnitude of the CO_2 evasion flux with
5 respect to the contemporary peatland C balance (see also Billett et al. 2010), and
6 question whether it should strictly be included in the NECB. The answer is catchment
7 specific and not simple. Even though some peatlands are characterised by biogenic,
8 isotopically young evasion CO_2 , the isotopic signatures of DOC and evasion CO_2
9 rarely match, suggesting there is a difference in their source, residence time and
10 transport rate to the stream system. Even when the ^{14}C content of DOC and evasion
11 CO_2 are isotopically young, the age of original C fixation varies and typically pre-
12 dates the contemporary atmosphere by up to about 13 years (e.g. Billett and others
13 2012b). Hence in terms of C fluxes and turnover, the aquatic and land-atmosphere
14 systems are not synchronised, to an extent that the annual NECB will inevitably
15 include flux terms that are operating at different timescales (Fig. 3). This implies that
16 there may be significant lags in the components that make up the C balance of a
17 peatland, with parts of the C cycle responding at different rates to change.

18 These differences become greater in peatland sites where both old (pre-
19 AD1955) biogenic and geogenic CO_2 from deep sources degas from stream surfaces.
20 In these systems it is difficult to justify (both in terms of age and origin) the inclusion
21 of the evasion flux in the contemporary NECB, although it could be justified in a C
22 accounting exercise as an additional emission source. The answer is, however, not
23 unequivocal because the isotopic signature of evasion CO_2 may comprise multiple
24 sources of differing ages and we do not rule out the presence of modern C that will
25 dilute an older ^{14}C - CO_2 signal. Whilst ^{14}C dating of CO_2 does not provide a precise

1 age for these different sources or their relative importance, ^{14}C concentrations >100%
2 modern must contain C fixed from the atmosphere since AD1955, and concentrations
3 <100% modern unequivocally demonstrate the presence of C fixed before AD1955.
4 Isotopic evidence from the aquatic pathway therefore suggests we may need to rethink
5 the way we understand or interpret the NECB, although the extent of the rethink will
6 vary from peatland to peatland.

7

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16

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23 interface in peatland streams. Although the size of the 3 evasion
24 sources are similar in this diagram, they will vary from peatland to peatland
25 and be reflected in different isotopic signatures

Table 1

Site	Catchment Area (km²)	Annual Precipitation (mm)	Elevation Range (m)	Discharge and range (Ls⁻¹)
<i>Loch More</i>	4.24	1129	121-195	36 (1-332)
<i>Auchencorth Moss</i>	3.35	1155	248-300	14 (3-93)
<i>Rough Sike</i>	0.83	1980	565-746	12 (6-114)
<i>Cottage Hill Sike</i>	0.17	1980	545-580	5 (2-188)
<i>Bleaklow</i>	1.39	1200	447-578	11 (10-12)
<i>Conwy</i>	1.24	2200	454-514	108 (3-374)
<i>Hafren</i>	0.93	2726	535-635	50 (9-75)

Table 2

Concentration (mg C L ⁻¹)				Flux (mg C ha ⁻¹ catchment s ⁻¹)			
	<i>Mean</i>	<i>SD</i>	<i>Median</i>	<i>Downstream</i>	<i>Mean</i>	<i>SD</i>	<i>Median</i>
<i>DOC</i>	14.1	8.4	12.5	<i>DOC</i>	9.24	28.56	1.79
<i>DIC</i>	3.8	6.0	2.7	<i>DIC</i>	1.82	6.06	0.28
<i>CO₂-C</i>	1.4	1.1	1.1	<i>CO₂-C</i>	0.72	1.68	0.20
<i>CH₄-C</i>	0.010	0.025	0.003	<i>CH₄-C</i>	0.004	0.014	0.001
				<i>Evasion</i>			
				<i>CO₂-C</i>	7.38	15.34	2.71
				<i>CH₄-C</i>	0.030	0.081	0.003

Table 3

Site	<i>n</i>	<i>CO</i> ₂	<i>DOC</i>	Published DOC fluxes	Reference
<i>Loch More</i>	5	71.1 ±58.9	12.3 ±10.3	No data	
<i>Auchencorth</i>	8	9.2	7.5	26.9 (2 yr)	Billett et al. 2004
<i>Moss</i>		±3.2	±3.3	19.3 (5 yr)	Dinsmore et al. 2013
<i>Rough Sike</i>	7	20.3 ±13.1	13.4 ±6.7	29.0 (16 yr)	Dinsmore (unpubl)
<i>Cottage Hill Sike</i>	10	26.6 ±13.5	93.6 ±59.7	23.4 (15 yr) 57.5 (2 yr)	Billett et al. 2010 Holden et al. 2012
<i>Bleaklow</i>	4	18.9 ±9.7	2.3 ±0.6	16.0 (3 yr)	O'Brien et al. 2008
<i>Conwy</i>	8	9.3 ±3.5	28.9 ±12.4	19.3 (2 yr)	Billett et al. 2010
<i>Hafren</i>	7	21.8* ±7.0	5.2 ±1.4	8.4 (2 yr)	Dawson et al. 2002
Overall mean value	49	23.3 ±6.9	29.1 ±12.9	25.0	

Table 4

Site	$\delta^{13}\text{C}$		^{14}C	
	C-CO ₂	C-DOC	C-CO ₂	C-DOC
<i>Loch More</i> (n=8)	-17.5 (±2.17)	-28.2*** (±0.20)	96.30 (±9.27)	109.50** (±3.59)
<i>Auchencorth Moss</i> (n=10)	-23.7 (±2.81)	-28.3** (±0.39)	93.80 (±6.18)	104.00* (±3.88)
<i>Cottage Hill Sike</i> (n=11)	-18.6 (±2.07)	-28.1*** (±0.14)	96.90 (±2.62)	111.00*** (±2.41)
<i>Conwy</i> (n=8)	-19.6 (±1.00)	-28.5*** (±0.10)	100.90 (±1.25)	112.20*** (±0.83)
<i>Finland</i> (n=15)	-25.2 (±2.02)	-28.4*** (±0.15)	107.59 (±1.94)	111.11*** (±1.18)

Figure 1

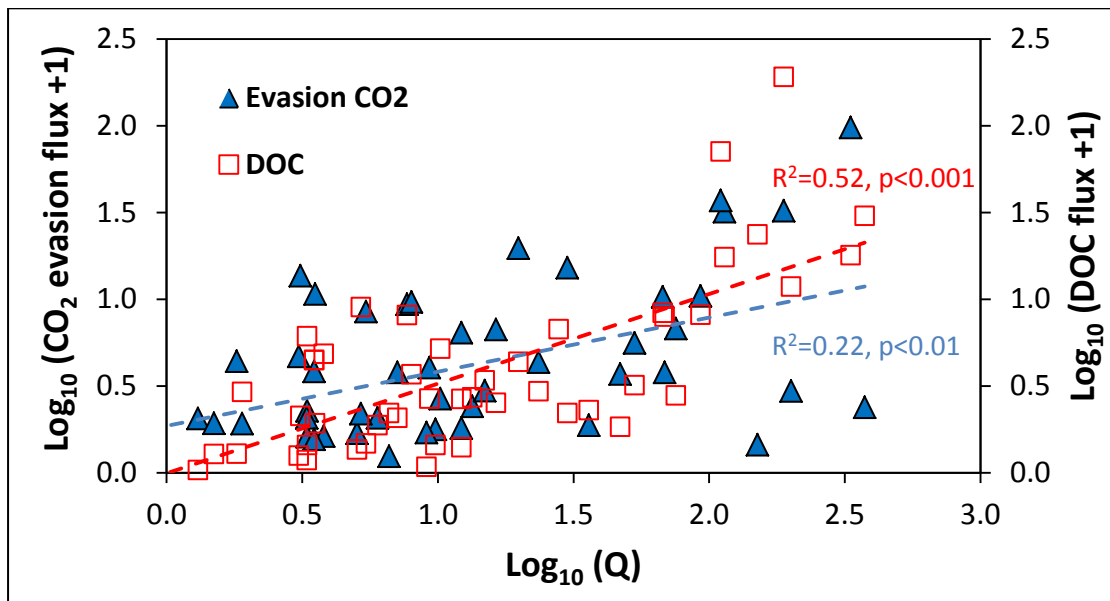


Figure 2

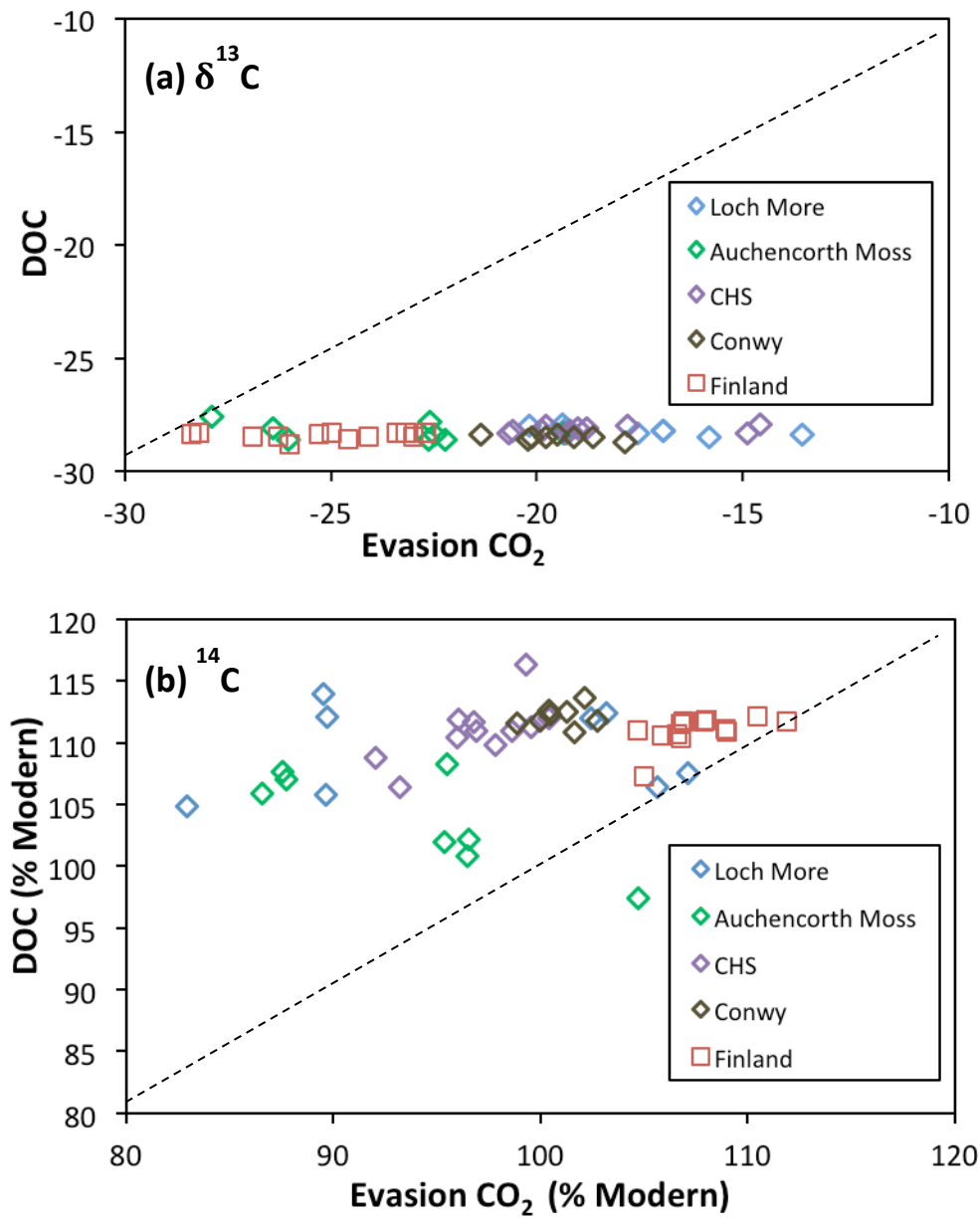


Figure 3

