Billett, M.F.; Garnett, M.H.; Dinsmore, K.J. 2015. Should aquatic CO2 evasion be included in contemporary carbon budgets for peatland ecosystems? *Ecosystems*, 18 (3). 471-480. 10.1007/s10021-014-9838-5

Should aquatic CO_2 evasion be included in contemporary carbon budgets for peatland ecosystems?

MF Billett[1,2], MH Garnett[3], KJ Dinsmore[2]

[1]Biological & Environmental Sciences, School of Natural Sciences, University of Stirling, Stirling, FK9 4LA, UK

[2] Centre for Ecology and Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK

[3]NERC Radiocarbon Facility, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, UK

Abstract

Quantifying the sink strength of northern hemisphere peatlands requires measurements or realistic estimates of all major C flux terms. Whilst assessments of the net ecosystem carbon balance (NECB) routinely include annual measurements of net ecosystem exchange and lateral fluxes of dissolved organic carbon (DOC), they rarely include estimates of evasion (degassing) of CO_2 and CH_4 from the water surface to the atmosphere, despite supersaturation being a consistent feature of peatland streams. Instantaneous gas exchange measurements from temperate UK peatland streams suggest that the CO_2 evasion fluxes scaled to the whole catchment are a significant component of the aquatic C flux (23.3±6.9 g C m^{-2} catchment yr^{-1}) and comparable in magnitude to the downstream DOC flux (29.1±12.9 g C m^{-2} catchment yr^{-1}). Inclusion of the evasion flux term in the NECB would be justified if evaded CO_2 and CH_4 were isotopically "young" and derived from a "within-ecosystem" source, such as peat or in-stream processing of DOC. Derivation from

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

1. Introduction

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

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

The fact that streams and rivers associated with peatland systems are consistently supersaturated with respect to CO_2 and CH_4 (Hope and others 2001; Dinsmore and Billett 2008; Wallin and others 2011) is a clear indication of the degassing potential of the aquatic system. Both gases are lost from the aquatic pathway as surface water gas concentrations progressively equilibrate with lower concentrations in the atmosphere. This has been demonstrated in downstream spatial measurements of $p\mathrm{CO}_2$ and $p\mathrm{CH}_4$ in which high concentrations are directly related to the spatial distribution of peat soils (Dawson and others 2002; Billett and Moore 2008) and where outgassing occurs in the proximity of source areas (Nilsson and others 2008). Measurements from the UK, N America and Sweden show that significant amounts of gas exchange occur across the water-air interface of peatland streams (Billett and Moore 2008; Billett and Harvey 2013; Wallin and others 2011). However, a lack of water-air flux measurements in small headwater streams has often led to the use of estimated or modelled values of gas transfer coefficients or velocities in regional upscaling (e.g. Teodoru and others 2009). Accurate flux estimates are also hindered by poor quantification of water surface area in low order streams. Hence there is still much uncertainty about the magnitude of the CO_2 evasion flux and its origin. This uncertainty has been recently improved by studies that show that K_{CO2} (the gas transfer coefficient of CO_2) can be predicted by a combination of slope and stream width/depth (Wallin and others 2011) or slope and stream velocity (Butman and Raymond 2011). In addition, the ability to measure CO_2 concentrations at higher temporal resolution has greatly improved understanding of aquatic CO_2 hydro-dynamics (Johnson and others 2010, Dinsmore and others 2013).

Whilst flux terms and the methods used to measure C exchange are well established for land-atmosphere gas exchange and downstream aquatic losses, evasion (degassing of CO_2 and CH_4 at the water surface) is less well understood and often poorly quantified or even worse, ignored. Most eddy covariance measurement systems exclude standing or flowing water and leave the evasion flux unmeasured (e.g. Billett and others 2004). Hence in a continental or global context the magnitude of the evasion flux is a major "unknown" (Cole and others 2007), although estimates for US streams and rivers suggest they release 97±32 Tg of C to the atmosphere each year (Butman and Raymond 2011). Globally it has been estimated that CO_2 evasion from inland waters is of similar magnitude to CO_2 uptake by the oceans (Tranvik and others 2009). In arctic lakes and streams it represents 25-50% of the net annual landscape carbon accumulation rate (Kling and others 1991). In the whole Yukon catchment (854,700 km^2) Striegl and others (2012) have estimated that gas emissions from the water surface account for 50% of the total lateral C export. Collectively these values suggest that the evasion flux represents an important loss of carbon and GHGs (greenhouse gases) from peatland ecosystems that include the aquatic pathway. Because the overall concept of the NECB is to assess the net rate of ecosystem C accumulation ("sink strength"), the inclusion of evasion CO_2 in NECB calculations will be justified if it is derived wholly from (1) lateral transport to the stream of "young" soil-derived CO_2, (2) within-stream decomposition of DOC and POC or (3) C fixed by within-stream photosynthesis. However, if CO_2 lost by evasion to the atmosphere is "old" and originates from outside the ecosystem boundary (for example, from a geogenic source or below the active rooting zone), inclusion in the NECB would not be justified and lead to an under-estimation of the current sink strength of peatland systems. Whilst "young and old" carbon could be defined in several ways, a chronological tool is required to provide an unambiguous definition. Here we measure the relative age of C based on it's radiocarbon concentration (Levin and Hesshaimer 2000); "young" C is defined as C fixed from the atmosphere post-AD1955 that is ^{14}C enriched (>100% modern) due to nuclear weapons testing (post-bomb); "old" or pre-bomb C is ^{14}C depleted and was fixed pre-AD1955. In addition, if the source of the CO_2 lost by evasion is both allochthonous and constitutes old stored carbon rather than young recently fixed/respired terrestrial carbon, contemporary NECB estimates would be influenced by carbon fixed during a different era. The concept of an NECB to assess carbon accumulation in terrestrial ecosystems is only useful when the timescales of C fixation are comparable and allow for interaction between individual components; hence it is important that non-contemporary C (for example derived from geological sources or peat produced more than 60 years ago) be excluded.

Here we aim to address the issue of inclusion of aquatic C in the NECB by firstly assessing the magnitude of the fluxes by comparing instantaneous measurements of CO_2 evasion and DOC fluxes from 6 UK peatland sites, and then producing estimates of catchment scale evasion fluxes using measurements of water surface area. We then uniquely combine C flux and dual isotope $\delta^{13}C$ and ^{14}C measurements from the same sites to answer the following questions; (1) is C evaded as CO_2 allochthonous (defined as aquatic C derived from terrestrial sources), or is it autochthonous (defined as aquatic C produced by in-stream C fixation), and (2) should evasion CO_2 be considered as part of the contemporary NECB of peatlands (we define contemporary in this case as our measurement period 2004-2008), or is it derived from an older (pre-AD1955) C pool?

2. Sites and Methods

Between 2004-2006 instantaneous aquatic C flux measurements were carried out in peatlands in Scotland (Loch More; Auchencorth Moss), northern England (Moor House; Bleaklow) and Wales (Migneint; Plynlimon). Catchment characteristics are summarised in Table 1. Seven 1st to 3rd order streams in total were studied, the Achscoriclate Burn (Loch More), Black Burn (Auchencorth Moss), Cottage Hill Sike and Rough Sike (both Moor House), Doctor’s Gate Clough (Bleaklow), Afon Ddu (Migneint) and Afon Hafren (Plynlimon). The host catchments vary in altitude and size from 121-746 m and 0.2-4.7 km^2, respectively with mean annual precipitation ranging from 1129 mm (Loch More, the most northerly site) to 2746 mm (Plynlimon, the most westerly site). Mean annual air temperature ranged from 5.3-10.0^{o}C. Peatland catchments are typically semi-natural and affected to varying degrees by low levels of (often seasonal) grazing and in some cases drainage. Hydrologically the streams are typically “flashy” with a rapid rainfall-runoff response and a wide range in discharge values (Table 1). Streamwater chemistry is characterised by low pH, low Ca and high DOC concentrations (Billett et al. 2007). For further details of the 7 streams refer to Billett and Harvey (2013).

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

$$\text{Instantaneous evasion flux (mg C m}^{-2}\text{ s}^{-1}\text{)} = \frac{\Delta_{CO2}\ (\Delta_{CH4})\ \text{x}\ K_{CO2}\ (K_{CH4})\ \text{x}\ \tau\ \text{x}\ Q}{R}$$

where Δ_{CO2} or Δ_{CH4} is the difference in the dissolved gas concentrations in the study reach if the stream was at atmospheric equilibrium (mg C L^{-1}), K_{CO2} or K_{CH4} is the gas transfer coefficient (min^{-1}), τ is the reach length travel time (min), Q is the average reach discharge (L s^{-1}) measured on each occasion at both ends of the study reaches using either a continuous or pulse injection of NaCl tracer, and R the water surface area of the reach (m^2). Full details of the methodology and flux calculations are given in Billett and Harvey (2013).

Dissolved CO_2 and CH_4 were measured directly at both ends of the study reach using headspace analysis (Kling and others 1991; Hope and others 1995; Hope and others 2001). This technique requires measurement of ambient atmospheric CO_2/CH_4 concentration, stream temperature, atmospheric pressure and elevation above mean sea level. A HP5890 Series II with Flame Ionisation Detector (FID) and attached methaniser was used to determine CO_2 and CH_4 concentrations (CO_2 and CH_4 detection limits 10 ppmv and 70 ppbv, respectively). Two filtered (0.45 µm PTFE) water samples (60 ml) were collected for the determination of DOC concentration. After sample acidification and sparging with N_2, DOC concentration was determined by digestion/uv oxidation using a Rosemount Dohrman DC-80 TOC Analyser (detection limit 0.1 mg L^{-1}; precision ± 0.04 mg L^{-1}). DIC concentration was calculated from the difference between the concentration of total dissolved carbon (DOC+DIC) in an unacidified sample and DOC concentration.

Instantaneous CO_2 and CH_4 (vertical) evasion fluxes (mg C m^{-2} s^{-1}) were compared to the lateral (downstream) flux of various C species (DOC, DIC, CO_2 and CH_4) by expressing all flux rates per unit area of catchment (mg C ha^{-1} catchment s^{-1}). Downstream fluxes were calculated by multiplying concentration (µg or mg C L^{-1}) by flow (L s^{-1}) and dividing by the catchment area upstream of the sample point. For evasion we make the simplifying assumption that the measured evasion rate was representative of the upstream channel area. Although we made evasion measurements along 2 representative reaches in the middle and lower sections of each stream, we know that evasion rate has high spatial variability (see Billett & Harvey 2013 for individual measurements). Then we calculated the water surface area in each catchment from the active drainage area length (including all flowing tributaries) and the average width of all the streams/tributaries within the drainage system. The former was calculated from detailed base maps and ground truthing, the latter by multiple measurements (10 m spacing) of stream width in the field. Catchment-scale evasion rates (allowing comparison with downstream C fluxes) were calculated as follows:

$$CO_2 \text{ or } CH_4 \text{ evasion flux (mg C ha}^{-1}\text{ catchment s}^{-1}) = \frac{\text{Instantaneous flux (mg C m}^{-2}\text{ s}^{-1}) \times \text{catchment water surface area (ha)}}{\text{upstream catchment area (ha)}}$$

Simultaneous measurements of the $\delta^{13}C$ and ^{14}C content of evasion CO_2-C and DOC-C were carried out on several of the UK peatland streams as well as 2 headwater streams in Finnish peatlands. Sufficient evasion CO_2 for ^{14}C analysis by accelerator mass spectrometry (AMS) was collected directly in the field using a molecular sieve linked to a floating chamber. The ^{14}C content of DOC was determined from 1L water samples that were subsequently filtered and freeze dried. For further details of the methodology see Billett and others 2007; Billett and others 2012a; Billett and others 2012b).

3. Results and Discussion

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

Both catchment scale CO_2 evasion and DOC fluxes were similar and significantly related to flow, although the relationship between discharge and DOC flux was strongest (Fig. 1). Our catchment-scale evasion rates are likely to underestimate the size of the overall flux because, whilst they include hydrological variability, they only include a small degree of spatial variability and exclude the source areas that are often associated with high pCO_2 and pCH_4 (e.g. Nilsson and others 2008). If the data from all sites are considered collectively the CO_2 evasion flux (7.38±15.34 mg C ha^{-1} catchment s^{-1}) was equivalent to the downstream export of DOC (9.24±28.56 mg C ha^{-1} catchment s^{-1}) and 10x larger than the downstream (lateral) export of CO_2-C (Table 2). Overall median CO_2-C evasion fluxes were higher than the median DOC fluxes at the sites. Fluxes of CH_4 (either as evasion or downstream export) were more than 2 orders of magnitude lower than the equivalent CO_2 flux.

The values presented in Fig. 1 can be used to make a first approximation of fluxes from each individual catchments (Table 3), although the small number of measurements for each catchment means that individual values have to be treated with a degree of caution. Despite this caveat, annual upscaled CO_2 evasion fluxes for individual catchments were in the range 9-27 g C m^{-2} catchment yr^{-1} and DOC fluxes in the range 2-29 g C m^{-2} catchment yr^{-1}; only the Hafren catchment showed a significant difference between flux values. We derive overall annual CO_2 evasion and DOC flux values from all our peatland headwater streams of 23.3±6.9 and 29.1±12.9 g C m^{-2} catchmment yr^{-1}, respectively (Table 3). We compared these values to published DOC fluxes from 6 of the sites derived from long-term datasets (2 to 16 yr) based on a weekly or 2 weekly sampling frequency (Table 2). Both our overall CO_2 evasion and DOC fluxes were comparable to the long-term published DOC flux value (25.0 g C m^{-2} catchment yr^{-1}) derived from all the sites (Table 3). We are therefore confident that the overall flux values derived from a relatively small number of individual measurements in the 7 catchments, were representative of the peatland system in terms of its inherent variability associated with discharge and season.

Whilst several recent studies (e.g. Wallin and others 2013) have also demonstrated the similarity in catchment-scale CO_2 evasion and DOC fluxes from peatland headwater streams and therefore highlight the importance of the aquatic pathway as a significant catchment carbon loss, relatively little is known about the source of the evaded CO_2 and whether it should be included in calculations of the contemporaneous NECB. We carried out concurrent dual isotope measurements ($\delta^{13}C$ and ^{14}C) of both evasion CO_2-C and DOC-C at 4 of the temperate UK peatland sites described above (Billett and others 2007; Billett and others 2012a) as well as in 2 boreal forested peatland headwater streams in N Karelia, Finland (Billett and others 2012b). Here for the first time we bring the isotope (Fig. 2, Table 4) and flux data together and use it to compare the age and source of both C species. The evasion isotope values have been corrected to account for CO_2 degassing into a closed collection chamber (Billett and Garnett 2010).

Evasion CO_2 was consistently and significantly more ^{13}C enriched than DOC in all 5 peatland catchments, with only 3 pairs of samples (total = 52) exhibiting similar $\delta^{13}C$ values (-27.6 to -28.4 ‰). Individual catchments were characterised by a specific range in $\delta^{13}C$-CO_2, with the Finnish sites being the most ^{13}C depleted and the Loch More (UK) sites the most ^{13}C enriched. The source, or more likely sources, of evasion CO_2 are therefore different from DOC, with the former derived either from decomposition of C3 plant material ($\delta^{13}C \approx -28$ ‰), atmospheric CO_2 ($\delta^{13}C \approx -8$ ‰), geological weathering ($\delta^{13}C \approx 0$ ‰) or CO_2 resulting from anaerobic fermentation ($\delta^{13}C \approx -14$ to $+10$ ‰) (Billett and others 2007; Billett and others 2012a). Compared to CO_2, $\delta^{13}C$-DOC values varied little and were consistent with a single source, namely decomposition of organic matter derived from C3 plants.

At all sites DOC was consistently and significantly more ^{14}C enriched than evasion CO_2 with individual catchments characterised by a distinct clustering of values (Fig. 2). With one exception (Auchencorth Moss), the radiocarbon content of DOC samples was young and close to the contemporary atmospheric value (107-105 % modern, estimated from Levin and Kromer 2004) for the time of sampling (2004-2008). These observations indicate that the DOC contained a substantial component of post-bomb C (i.e. carbon originally fixed after AD1955). The most ^{14}C enriched CO_2 samples were from N Karelia, Finland (mean 107.69±1.94 % modern), which again indicated that this CO_2 was radiogenically young and substantially derived from carbon fixed during the post-bomb era. In contrast, CO_2 from most UK sites had ^{14}C concentrations <100 %modern, reflecting a component of old pre-bomb carbon (i.e. carbon fixed before ~AD1955); the most ^{14}C depleted (i.e. oldest) CO_2 was from Loch More (aged up to 1502±28 years BP) and Auchencorth Moss (aged up to 1163±29 years BP), however, all sites did at times provide CO_2 samples with ^{14}C concentrations >100 %modern, indicating younger post-bomb carbon.

The difference in the $\delta^{13}C$ and ^{14}C signatures of DOC and evasion CO_2 strongly suggest that a significant proportion of CO_2 lost by evasion is not derived from within-stream breakdown of DOC. A non-stream source in peatland systems is also supported by published non-isotopic data showing a strong link between temporal changes in soil atmosphere and stream CO_2 concentrations (Hope and others 2004; Dinsmore and Billett 2008). In addition, the isotopic signature of CO_2 evasion at most of the sites appears to have either a deeper biogenic (peat) or a geogenic (weathering) component and thus originates from outside the physical lower ecosystem boundary associated with the strict definition of the NECB (Chapin and others 2006). The timescales of geogenic CO_2 production versus contemporary carbon cycling also leads to challenges in interpreting the NECB, suggesting inclusion of this evaded CO_2 component may not be appropriate. There are peatland sites (e.g. Loch More and Auchencorth Moss) where the source and age of CO_2 and DOC are significantly different (Fig. 2) whilst there are others, such as the forested Finnish peatland sites, where the isotopic signatures are much closer and more characteristic of DOC and CO_2 produced from recently fixed C (Billett and others 2012b). Hence, whilst the isotopic data can be explained by a mixture of sources in most of these acidic low productivity systems, CO_2 evasion is likely to be primarily derived from non-stream sources. A similar conclusion was reached in the Yukon River and its tributaries, where Wickland and others (2012) found that biodegradation of soil-derived DOC only accounted for <6% of the total CO_2 emission from the water surface.

Compared to DOC, the source of evasion CO_2 varies significantly from peatland to peatland and we present evidence to show that old (pre-AD1955) CO_2 is being released into the atmosphere from a number of sites. This is significant because it suggests that the contemporary C balance of peatlands is being affected by the release of C from an older (pre-AD1955) and deeper (primarily sub-rooting zone) C pool, the contribution of which varies spatially between peatlands. Whilst DOC at these sites can almost exclusively be regarded as the result of turnover of young organic C, evasion CO_2 cannot be regarded solely as the breakdown product of recently fixed and respired terrestrial carbon. At the UK peatland sites there is strong evidence to suggest that the evaded CO_2 is derived from multiple sources including decomposition of deep peat (biogenic) and carbonate weathering (geogenic) (Billett and others 2007; Billett and others 2012a). We have recently shown that the age of aquatic dissolved CO_2 at the Auchencorth Moss catchment varied from 707 to 1210 years BP during a single hydrological year (Garnett and others 2012), with the oldest and youngest CO_2 associated with low (deep source) and high discharge (shallow source), respectively. Because the $\delta^{13}C$-CO_2 values were relatively constant (-23.0 to -24.2 ‰) the isotope data indicates that the CO_2 is predominantly derived from a single biogenic peat source that varies in depth during the hydrological year. The release of CO_2 of variable age and source from natural peatland pipes to the atmosphere (Billett and others 2012a) further supports the potential for the involvement of a deeper, old C pool in measurements of the contemporary C balance, originating from outside the ecosystem boundaries normally associated with the NECB.

4. Conclusions

Our best current estimate for the size of the evasion flux term from UK peatland headwater streams is 23.3 g C m^{-2} catchment yr^{-1}, which is of similar magnitude to the UK lateral DOC flux estimate of 19-27 g C m^{-2} catchment yr^{-1} for the same type of stream system (Billett and others 2010). Upscaled to a national level using a value of 24,640 km^2 for the UK peatland area (Billett and others 2010), we estimate that the CO_2 evasion flux from peatland streams represents an additional natural emission source of the order of 0.57 Mt C yr^{-1} to the atmosphere. Given the errors associated with the evasion estimate (Table 3) and the area of UK peatlands (values range from 17,500 km^2 to 32,830 km^2; Joosten & Clark 2002, JNCC 2011), the UK peatland CO_2 evasion emission value could range from 0.29-0.99 Mt C yr^{-1}. To put this into context Hope and others (1997) and Worrall and others (2012) have independently estimated a total DOC loss from British rivers to tidal waters of 0.68±0.07 Mt C yr^{-1} and 0.91±0.35 Mt C yr^{-1}, respectively. The value of 0.57 Mt C yr^{-1} is higher than that estimated for the loss of C from the drainage of UK fenlands (0.5 Mt C yr^{-1}) and from peat extraction (0.2 Mt C yr^{-1}) (Cannell and others 1999).

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

These differences become greater in peatland sites where both old (pre-AD1955) biogenic and geogenic CO_2 from deep sources degas from stream surfaces. In these systems it is difficult to justify (both in terms of age and origin) the inclusion of the evasion flux in the contemporary NECB, although it could be justified in a C accounting exercise as an additional emission source. The answer is, however, not unequivocal because the isotopic signature of evasion CO_2 may comprise multiple sources of differing ages and we do not rule out the presence of modern C that will dilute an older ^{14}C-CO_2 signal. Whilst ^{14}C dating of CO_2 does not provide a precise age for these different sources or their relative importance, ^{14}C concentrations >100% modern must contain C fixed from the atmosphere since AD1955, and concentrations <100% modern unequivocally demonstrate the presence of C fixed before AD1955. Isotopic evidence from the aquatic pathway therefore suggests we may need to rethink the way we understand or interpret the NECB, although the extent of the rethink will vary from peatland to peatland.

Acknowledgements

The research reported here was funded primarily by a UK NERC Advanced Research Fellowship (NER/J/S/2002/00647) with additional NERC Radiocarbon Facility allocations (1093.1004, 1158.1005, 1260.1007, 1380.0409). The various UK landowners are thanked for allowing access to the study sites and METLA (Finnish Forestry Research Institute) for providing logistical support for fieldwork in Finland. The authors thank the three anonymous reviewers and the Subject Matter Editor for their constructively critical review of the manuscript.

References

Billett MF, Palmer SM, Hope D, Deacon C, Storeton-West R, Hargreaves KJ, Flechard C, Fowler D (2004), Linking land-atmosphere-stream carbon fluxes in a lowland peatland system, Glob Biogeochem Cycle 18:GB1024.

Billett MF, Garnett MH, Harvey F. 2007. UK peatland streams release old carbon dioxide to the atmosphere and young dissolved organic carbon to rivers. Geophys Res Lett 34 :L23401.

Billett MF, Moore TR. 2008. Supersaturation and evasion of CO_2 and CH_4 in surface waters at Mer Bleue Peatland, Canada. Hydrol Proc 22:2044–2054.

Billett MF, Charman DJ, Clark JM, Evans CD, Evans MG, Ostle NJ, Worrall F, Burden A, Dinsmore KJ, Jones T, McNamara NP, Parry L, Rowson JG, Rose R. 2010. Carbon balance of UK peatlands: current state of knowledge and future research challenges. Clim Res 45:13-29.

Billett MF, Garnett MH. 2010. The isotopic composition of CO_2 lost by evasion from surface water to the atmosphere: a methodological comparison of a direct and indirect approach. Limnol Oceanog Methods 8:45-53.

Billett MF, Dinsmore KJ, Garnett MH, Smart RP, Holden J, Baird AJ, Chapman, PJ. 2012a. Variable source and age of different forms of carbon released from natural peatland pipes. JGR Biogeosciences 117:G02003.

Billett MF, Garnett MH, Dinsmore KJ, Dyson KE, Harvey F, Thomson AH, Piirainen S, Kortelainen P. 2012b. Age and source of different forms of carbon released from boreal peatland streams during spring snowmelt in E. Finland. Biogeochem 111:273-286.

Billett MF, Harvey FH. 2013. Measurements of CO_2 and CH_4 evasion from UK peatland headwater streams. Biogeochem 114:165-181.

Butman D, Raymond PA. 2011. Significant efflux of carbon dioxide from streams and rivers in the United States, Nature Geosci 4:839-842.

Cannell, MGR, Milne R, Hargreaves KJ, Brown TAW, Cruickshank, MM, Bradley RI, Spencer T, Hope D, Billett MF, Adger WN, Subak S. 1999. National inventories of terrestrial carbon sources and sinks: The U.K. experience, Clim Change 42:505–530.

Chapin FS III, Woodwell GM, Randerson JT Rastetter EB, Lovett GM, Baldocchi DD, Clark DA, Harmon ME, Schimel DS, Valentini R, Wirth C,Aber JD, Cole JJ, Goulden ML, Harden JW, Heimann M, Howarth RW, Matson PA, McGuire AD, Melillo JM, Mooney HA, Neff JC, Houghton RA, Pace ML, Ryan MG, Running SW, Sala OE, Schlesinger WH, Schulze ED. 2006. Reconciling carbon-cycle concepts terminology, and methods. Ecosystems 9:1041–1050.

Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing JA, Middelburg JJ, Melack J. 2007. Plumbing the Ecosystems 10:171-184.

Dawson JJC, Billett MF, Neal C, Hill S. 2002. A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. J Hydrol 257:226-246.

Dinsmore KJ, Billett MF. 2008. Continuous measurement and modelling of CO_2 losses from a peatland stream during stormflow events. Water Resour Res 44:W12417.

Dinsmore KJ, Billett MF, Skiba U, Rees RM, Drewer J, Helfter C. 2010. Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment. Global Change Biol 16:2750-2762.

Dinsmore KJ, Wallin MB, Johnson MS, Billett MF, Bishop K, Pumpanen J, Ojala A. 2013. Contrasting CO_2 concentration discharge dynamics in headwater streams: A multi-catchment comparison. 2013 J Geophy Res – Biogeosciences 118:445-461.

Garnett MH, Dinsmore KJ, Billett MF. 2012. Annual variability in the radiocarbon age and source of dissolved CO_2 in a peatland stream. SciTotal Environ 427-428:277-285.

Gorham E. 1991. Northern peatlands: Role in the carbon cycle and probable responses to climatic warming, Ecol Appl 1:182–195.

Hope D, Palmer SM, Billett MF, Dawson JJC. 2001. Carbon dioxide and methane evasion from a temperate peatland stream. Limnol Oceanog 46:847-857.

Hope D, Palmer SM, Billett MF, Dawson JJC. 2004. Variations in dissolved CO_2 and CH_4 in a first order stream and catchment: an investigation of soil stream. Hydrol Proc 18:3255-3275.

Hope D. Dawson JJC, Cresser MS, Billett MF. 1995. A method for measuring free-CO_2 in upland streamwater using headspace analysis. J Hydrol 166:1–14.

Hope D, Billett MF, Milne R, Brown TAW. 1997. Exports of organic carbon in British rivers. Hydrol Proc 11:325–344.

IPCC. 2007. Technical Summary. In Climate Change 2007: The Physical Science Basis. Contribution of Working Group 1 to the Forth Assessment Report of the Intergovernmental Panel on Climate Change, edited by Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

JNCC. 2011. Towards an Assessment of the State of UK Peatlands. Joint Nature Conservation Committee Report No. 445, ISSN 0963 8901.

Johnson MS, Billett MF, Dinsmore KJ, Wallin M, Dyson K. 2010. Direct in situ measurement of dissolved carbon dioxide in freshwater aquatic systems – method and applications. Ecohydrol 3:68-78.

Joosten H, Clarke D. 2002. Wise use of mires and peatlands. International Mire Conservation Group and International Peat Society, ISBN 951-97744-8-3.

Kling GW, Kipphut GW, Miller MC. 1991. Arctic streams and lakes as conduits to the atmosphere: Implications for tundra carbon budgets. Science 251:298-301.

Koehler AK, Sottocornola M, Kiely G. 2011. How strong is the current carbon sequestration of an Atlantic blanket bog? Global Change Biol 17:309–319, doi: 10.1111/j.1365-2486.2010.02180.x

Levin I, Hasshaimer V. 2000. Radiocarbon – A unique tracer of global carbon cycle dynamics. Radiocarbon 42:69-80.

Neal C, House WA, Down C. 1998. An assessment of excess carbon dioxide partial pressures in natural waters based on pH and alkalinity measurements. Sci Total Environ 210–211:173–185.

Nilsson M, Sagerfors J. Buffam I. Laudon H, Eriksson T, Grelle A, Klemedtsson L, Weslien P, Lindroth A (2008) Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire - a significant sink after accounting for all C-fluxes. Glob Change Biol 14:2317-2332.

Roulet N, Lafleur PM, Richard PJH, Moore TR, Humphreys ER, Bubier J. 2007. Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. Global Change Biol 13:397–411.

Striegl RG, Dornblaser MM, McDonald CP, Rover JR, Stets EG. 2012. Carbon dioxide and methane emissions from the Yukon River system. Global Biogeochem Cycles 26:GB0E05.

Teodoru C R, Del Giorgio PA, Prairie YT, Camire M. 2009. Patterns in pCO_2 in boreal streams and rivers of northern Quebec, Canada. Global Biogeochem Cycles 23:GB2012.

Tranvik LJ, Downing JA, Cotner JB, Loiselle SA, Striegl RG, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB, Kortelainen PL, Kutser T, Larsen S, Laurion I, Leech DM, McCallister SL, McKnight DM, Melack JM, Overholt E, Porter JA, Prairie Y, Renwick WH, Roland F, Sherman BS, Schindler DW, Sobek S, Tremblay A, Vanni MJ, Verschoor AM, von Wachenfeldt E, Weyhenmeyer

GA. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol Oceanog 54:2298–2314.

Turunen J, Tomppo E, Tolonen K, Reinikainen A. 2002. Estimating carbon accumulation rates of undrained mires in Finland – application to boreal and subarctic regions. Holocene 12:69–80.

Wallin MB, Öquist MG, Buffam I, Billett MF, Nisell J, Bishop KH. 2011. Spatiotemporal variability of the gas transfer coefficient (KCO_2) in boreal streams; implications for large scale estimates of CO_2 evasion. Global Biogeochem Cycles 25:GB3025.

Wallin MB, Grabs T, Buffam I, Laudon H, Ågren A, Öquist M.G, Bishop KH. 2013. Evasion of CO_2 from streams – The dominant component of the carbon export through the aquatic conduit in a boreal landscape. Global Change Biol 19:785–797.

Wickland K P, Aiken GR, Butler K, Dornblaser MM, Spencer RGM, Striegl RG. 2012. Biodegradability of dissolved organic carbon in the Yukon River and its tributaries: Seasonality and importance of inorganic nitrogen. Global Biogeochem Cycles 26:GB0E03.

Worrall F, Davis H, Bhogal A, Lilly A, Evans M, Turner K, Burt T, Barraclough D, Smith P, Merrington G. 2012. The flux of DOC from the UK - Predicting the role of soils, land use and net watershed losses. J Hydrol 448:149-160.

List of Tables

Table 1: General characteristics of the study catchments (median discharge values are for the lowest downstream site at the time of sampling)

Table 2: Overall mean, standard deviation and median (n=49) concentration and instantaneous aquatic carbon flux values

Table 3: Mean (±SE) annual evasion CO_2 and lateral DOC fluxes (g C m^{-2} catchment yr^{-1}) from the study catchments. The measurement period for the published DOC fluxes are in parentheses. A significant difference (paired t-test) between catchment CO_2 evasion and DOC fluxes is shown by *($p \leq 0.05$)

Table 4: Mean $\delta^{13}C$-CO_2, $\delta^{13}C$-DOC, ^{14}C-CO_2 and ^{14}C-DOC (±SD) of evasion CO_2 and stream DOC at sites in the UK and Finland. ^{14}C values are expressed in % modern. A significant differences (paired t-test) between the isotopic composition of CO_2 and DOC ($\delta^{13}C$ and ^{14}C) in individual catchments is shown by ***($p \leq 0.001$), **($p \leq 0.01$) and *($p \leq 0.05$)

List of Figures

Figure 1: Instantaneous CO_2 and DOC fluxes (mg C ha^{-1} catchment s^{-1}) as a function of discharge (Ls^{-1}). The red and blue regression lines are for DOC and evasion CO_2, respectively

Figure 2: Relationship between (a) $\delta^{13}C$ and (b) ^{14}C for DOC and evasion CO_2

Figure 3: Conceptual diagram to illustrate the origins, flux pathways and multiple timescales associated with the evasion of CO_2 at the water-atmosphere interface in peatland streams. Although the size of the 3 evasion sources are similar in this diagram, they will vary from peatland to peatland and be reflected in different isotopic signatures

Table 1

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

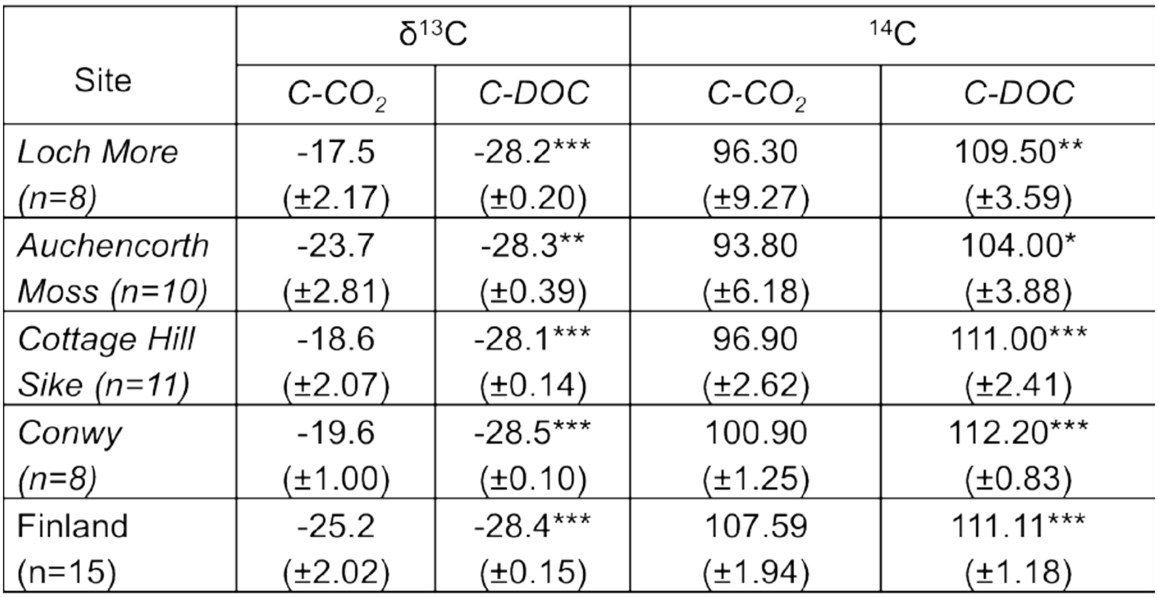
Table 2

Concentration (mg C L^{-1})				**Flux (mg C ha^{-1} catchment s^{-1})**			
	Mean	*SD*	*Median*	*Downstream*	*Mean*	*SD*	*Median*
DOC	14.1	8.4	12.5	*DOC*	9.24	28.56	1.79
DIC	3.8	6.0	2.7	*DIC*	1.82	6.06	0.28
CO_2-C	1.4	1.1	1.1	CO_2-C	0.72	1.68	0.20
CH_4-C	0.010	0.025	0.003	CH_4-C	0.004	0.014	0.001
				Evasion			
				CO_2-C	7.38	15.34	2.71
				CH_4-C	0.030	0.081	0.003

Table 3

Site	***n***	***CO_2***	***DOC***	**Published DOC fluxes**	**Reference**
Loch More	5	71.1 ±58.9	12.3 ±10.3	No data	
Auchencorth Moss	8	9.2 ±3.2	7.5 ±3.3	26.9 (2 yr) 19.3 (5 yr)	Billett et al. 2004 Dinsmore et al. 2013
Rough Sike	7	20.3 ±13.1	13.4 ±6.7	29.0 (16 yr)	Dinsmore (unpubl)
Cottage Hill Sike	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
Bleaklow	4	18.9 ±9.7	2.3 ±0.6	16.0 (3 yr)	O'Brien et al. 2008
Conwy	8	9.3 ±3.5	28.9 ±12.4	19.3 (2 yr)	Billett et al. 2010
Hafren	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	$\delta^{13}C$		^{14}C	
	C-CO$_2$	*C-DOC*	*C-CO$_2$*	*C-DOC*
Loch More (n=8)	-17.5 (±2.17)	-28.2*** (±0.20)	96.30 (±9.27)	109.50** (±3.59)
Auchencorth Moss (n=10)	-23.7 (±2.81)	-28.3** (±0.39)	93.80 (±6.18)	104.00* (±3.88)
Cottage Hill Sike (n=11)	-18.6 (±2.07)	-28.1*** (±0.14)	96.90 (±2.62)	111.00*** (±2.41)
Conwy (n=8)	-19.6 (±1.00)	-28.5*** (±0.10)	100.90 (±1.25)	112.20*** (±0.83)
Finland (n=15)	-25.2 (±2.02)	-28.4*** (±0.15)	107.59 (±1.94)	111.11*** (±1.18)

Figure 1

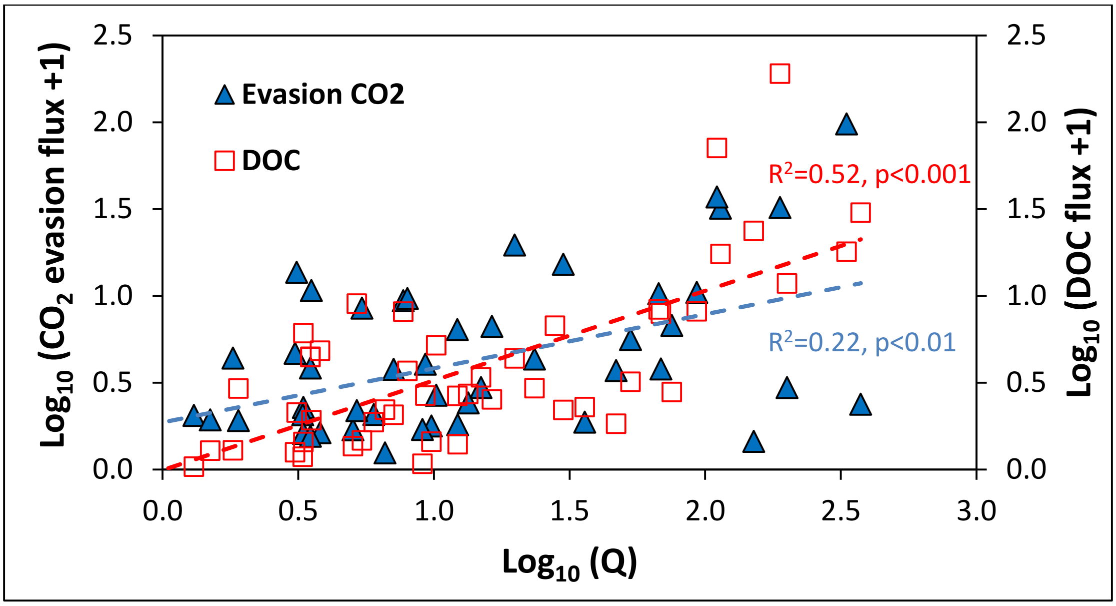

2.5
2.0
1.5
1.0
0.5
0.0
Log$_{10}$ (CO$_2$ evasion flux +1)
Evasion CO2
DOC
R^2=0.52, p<0.001
R^2=0.22, p<0.01
Log$_{10}$ (DOC flux +1)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Log$_{10}$ (Q)

Figure 2

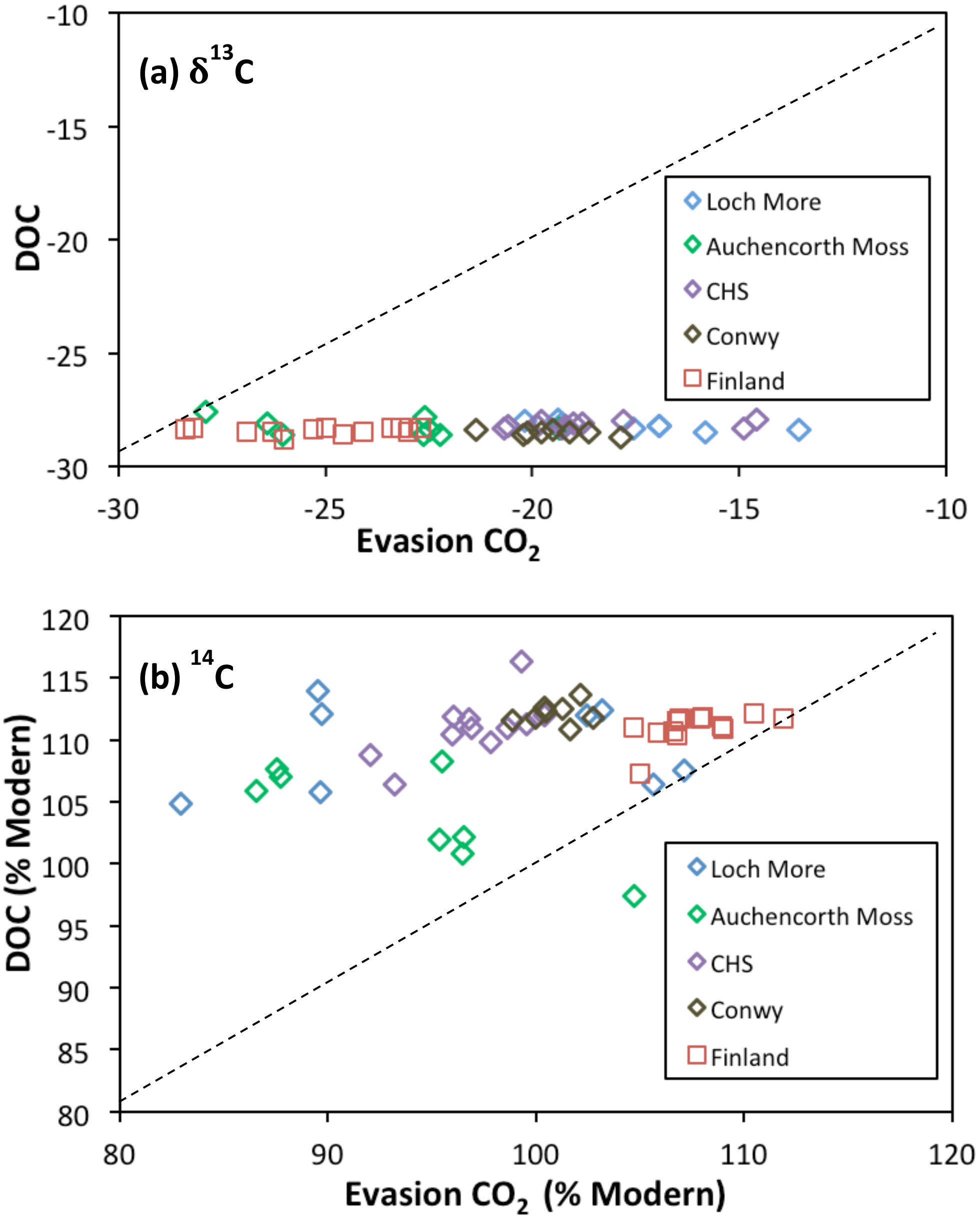
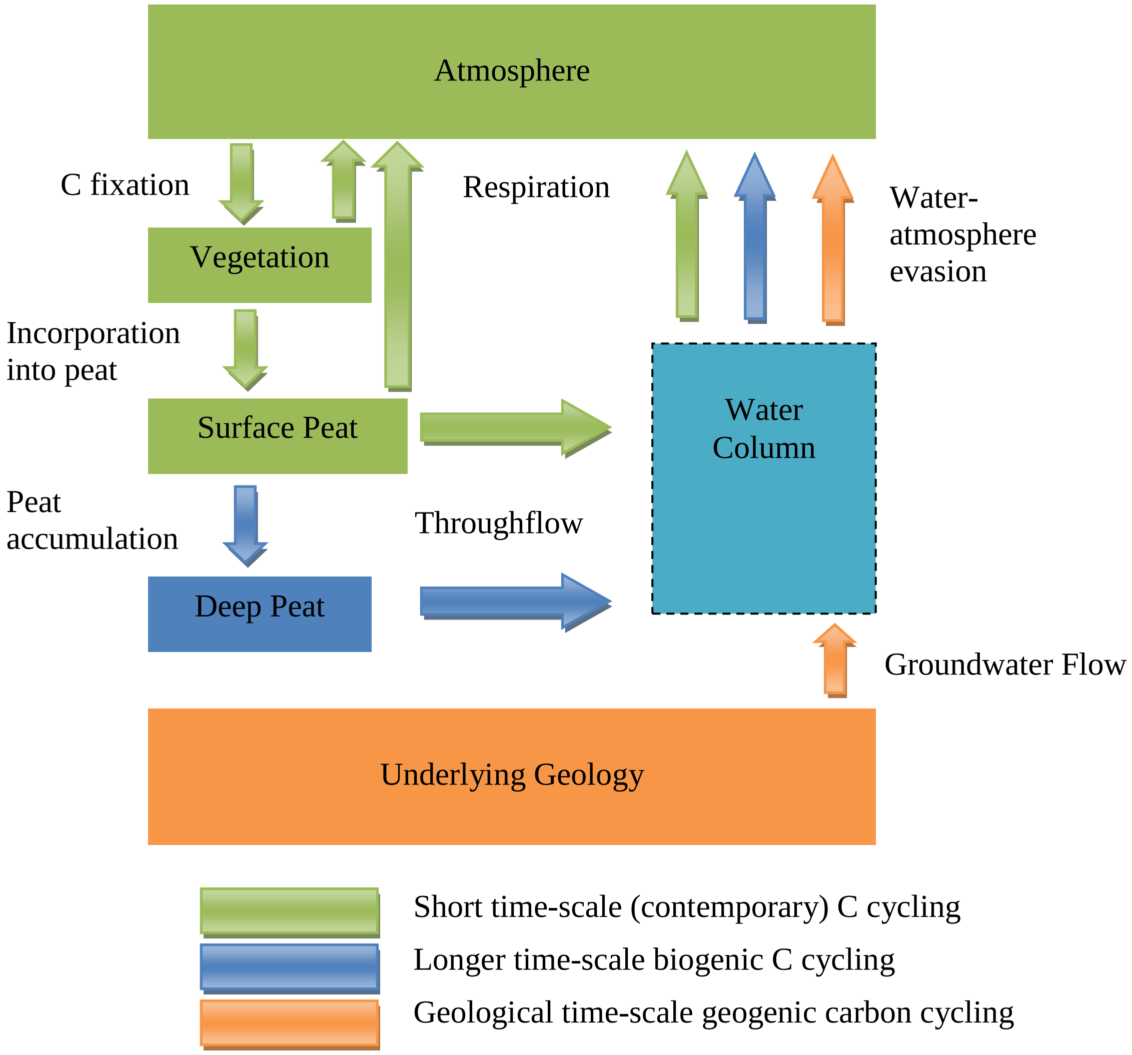

(a) δ13C
DOC
-10
-15
-20
-25
-30
-30
-25
-20
-15
-10
Evasion CO2
Loch More
Auchencorth Moss
CHS
Conwy
Finland
(b) 14C
DOC (% Modern)
120
115
110
105
100
95
90
85
80
80
90
100
110
120
Evasion CO2 (% Modern)
Loch More
Auchencorth Moss
CHS
Conwy
Finland

Figure 3


Atmosphere
C fixation
Respiration
Vegetation
Water-
atmosphere
evasion
Incorporation
into peat
Surface Peat
Water
Column
Peat
accumulation
Throughflow
Deep Peat
Groundwater Flow
Underlying Geology
Short time-scale (contemporary) C cycling
Longer time-scale biogenic C cycling
Geological time-scale geogenic carbon cycling