Annual variability in the radiocarbon age and source of dissolved CO2 in a peatland stream

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ABSTRACT

Radiocarbon dating has the capacity to significantly improve our understanding of the aquatic carbon cycle. In this study we used a new passive sampler to measure the radiocarbon (\(^{14}\)C) and stable carbon (\(\delta^{13}\)C) isotopic composition of dissolved CO2 for the first time in a peatland stream throughout a complete year (May 2010 – June 2011). The in-stream sampling system collected time-integrated samples of CO2 continuously over approximately one month periods. The rate of CO2 trapping was proportional to independently measured streamwater CO2 concentrations, demonstrating that passive samplers can be used to estimate the time-averaged dissolved CO2 concentration of streamwater. While there was little variation and no clear trend in \(\delta^{13}\)CO2 values (suggesting a consistent CO2 source), we found a clear temporal pattern in the \(^{14}\)C concentration of dissolved CO2. The \(^{14}\)C age of CO2 varied from 707±35 to 1210±39 years BP, with the youngest CO2 in the autumn and oldest in spring/early summer. Mean stream discharge and \(^{14}\)C content of dissolved CO2 were positively correlated. We suggest that the observed pattern in the \(^{14}\)C content of dissolved CO2 reflects changes in its origin, with older carbon derived from deeper parts of the peat profile contributing proportionally more gaseous carbon during periods of low stream flow.

Keywords
Carbon dioxide, Radiocarbon, Peatland, Streams, Carbon

1. Introduction

Peatland formation has produced a global terrestrial carbon store of approximately the same size as the current atmospheric carbon pool (Clymo and Bryant, 2008). Considerable research effort is now being focussed on the effect of man and climatic variability on this important terrestrial carbon store involving a combination of flux measurements and process-based studies (e.g. Billett et al., 2010). Drainage waters are increasingly being recognised as important conduits for carbon release from peatlands, and are now known to represent an important flux term in the annual carbon balance (Dinsmore et al., 2010; Koehler et al., 2011).
Organic-rich surface waters draining peatlands are typically acidic and supersaturated with respect to CO$_2$ and CH$_4$ (e.g. Dawson et al., 1995; Billett and Moore, 2008). In these systems carbon exists in three main forms: POC (particulate organic carbon), DOC (dissolved organic carbon) and DIC (dissolved inorganic carbon) (Eatherall et al., 1998). For DIC, carbon in streamwater can exist in the form of carbonate, bi-carbonate, or dissolved CO$_2$, the proportion of which varies with pH and temperature according to the carbonate buffering system (Hope et al., 1995; Aufdenkampe et al., 2011).

In streams draining peatlands, where DIC is primarily present as CO$_2$ due to low pH, CO$_2$ supersaturation varies both spatially (Dawson et al., 1995; Dawson et al., 2001) and temporally (Dinsmore and Billett, 2008; Johnson et al., 2010). Degassing (evasion) of CO$_2$ from the water surfaces of peatlands and other saturated carbon-rich systems is known to represent an important emission pathway connecting the below-ground carbon store to the atmosphere (Kling et al., 1991; Dinsmore et al., 2011). Consequently, for a better assessment of the importance of peatland carbon fluxes, and their potential response to change (e.g. climate and/or management) a greater understanding is required of the size and source of CO$_2$ loss via peatland streams.

Radiocarbon ($^{14}$C) analysis can provide important information on the age and rate that carbon is cycled through various components of ecosystems. $^{14}$C dating of peat, or the constituents that form peat, has been widely used to reconstruct the development of peatlands and to quantify rates of carbon accumulation and loss (e.g. Clymo and Bryant, 2008). $^{14}$C analysis of waters draining peatlands has largely focussed on the age of the DOC component (e.g. Benner et al., 2004; Evans et al., 2007). For waters draining intact peatlands, DOC has typically been found to have $^{14}$C contents that exceed 100 %modern (Tipping et al., 2010), unambiguously indicating the presence of “bomb-$^{14}$C” (Levin and Hesshaimer, 2000).
Analysis of the $^{14}$C age of the DIC component (or its gaseous constituent, CO$_2$) transported by rivers has previously been undertaken using one of two methods: (1) an indirect method whereby water samples are collected in the field, returned to the laboratory and the entire DIC recovered as CO$_2$ by “gas-stripping” (e.g. Mayorga et al., 2005), or (2) a direct method whereby CO$_2$ evading from the water surface is captured using a floating chamber and adsorbed onto a molecular sieve, which can be subsequently processed in the laboratory to recover the CO$_2$ for isotope analysis (Billett et al., 2006; Billett and Garnett, 2010).

Studies using the chamber method have revealed that in UK peatlands CO$_2$ degassed from the water surface is often derived from a much older source (up to at least 1000 years BP) than the DOC component, and that its isotopic signature ($^{14}$C and $\delta^{13}$C) can vary considerably both temporally and spatially between and within catchments (Billett et al., 2007). This within-catchment variability in source and age has also been demonstrated for CO$_2$ released from peatland pipes (Billett et al., in press a), which are known to act as important point sources for greenhouse gas release from peatlands (Dinsmore et al., 2011). In contrast, CO$_2$ evaded from a Finnish stream during the spring thaw was predominantly derived from carbon fixed within recent decades, as evidenced by the substantial component of bomb-14C (Billett et al., in press b). Using the gas-stripping method, Mayorga et al. (2005) showed that the majority of CO$_2$ evaded from Amazon rivers was derived from young (< 5 years old) carbon sources.

Whilst both the direct and indirect methods for determining the $^{14}$C concentration of aquatic CO$_2$ have provided valuable insights, they both rely on the collection of samples over short periods of time. Consequently we currently do not know whether these ‘spot samples’ are representative of longer timescales or the full hydrograph range. One solution would be to increase the temporal resolution of sample collection, however, this is time-consuming and the cost of $^{14}$C analysis is likely to make this approach prohibitive. Recently, a new passive sampling method has been developed and tested for the collection of CO$_2$ for carbon isotope analysis from a range of environments including soil-respired CO$_2$ (Garnett et al., 2009),
atmospheric CO₂ (Garnett and Hartley, 2010) and dissolved CO₂ in water-logged peat (Garnett and Hardie, 2009). The approach is similar to the established passive sampling methods used to collect time-integrated solute samples in surface waters over periods of weeks or months (e.g. Vrana et al., 2005; Rozemeijer et al., 2010). The technique is suited for the collection of samples over extended sampling times (up to several months) and whilst it has previously been deployed to sample CO₂ from water-saturated soils, it has hitherto not been employed to sample dissolved CO₂ in stream waters. Here, we report for the first time a 12 month series of carbon isotope (¹⁴C and δ¹³C) analyses of dissolved CO₂ collected from a peatland stream using the passive sampling technique. The volume of CO₂ recovered and rate of CO₂ trapping are also reported. We relate these results to measurements of stream and climatic conditions and hypothesised that: i) the passive sampling method provides a reliable method for the collection of dissolved CO₂ from peatland drainage waters for carbon isotope analysis, and ii) that changes in the isotopic composition of streamwater dissolved CO₂ provides information on annual variability in source and age.

2. Methods

2.1. Study site and measurement of site characteristics

Sampling was performed in the Black Burn, a peatland stream draining Auchencorth Moss in central Scotland (55°47’34 N; 3°14’35W). The catchment has an area of 3.4 km², spans an altitude range of ~250-300 m asl, and contains 85% peatland with peat depths reaching >5 m (Dinsmore et al., 2010). The vegetation in the catchment is predominantly a mixture of grasses and sedges covering a basal layer of mosses associated with a hummock/hollow microtopography. The dominant bryophytes are Sphagnum and Polytrichum species and the main vascular plants Deschampsia flexuosa, Molinia caerulea, Festuca ovina, Eriophorum angustifolium, Eriophorum vaginatum, Juncus effusus, Juncus squarrosus and Calluna vulgaris (Dinsmore et al., 2009a). The area is the focus of a long-term study of carbon cycling (Billett et al., 2010; Dinsmore et al., 2010) and is one of the UK Centre for Ecology and Hydrology’s ‘Carbon Catchments’, with continuous measurement of particulate, dissolved...
and gaseous forms of aquatic carbon since 2006. Carbon isotopic composition of both dissolved organic carbon and CO₂ evading from the stream surface (Billett et al., 2006, 2007) has been previously characterised.

Discharge in the Black Burn is monitored at 15 minute intervals using an In-Situ Inc Level Troll® pressure transducer and rating curve produced from manual dilution gauging measurements ($r^2 = 0.88$); stream temperature was also provided by the Level Troll® sensor. Dissolved CO₂ concentrations were calculated from weekly headspace spot samples collected approximately 10 m downstream from the location of the CO₂ passive samplers throughout the study period. The headspace method involved equilibration of an ambient air volume (20 ml) with a stream water sample (40 ml) by vigorously shaking in a syringe for one minute at stream temperature. The equilibrated headspace was then transferred to a separate gas-tight syringe and analysed, alongside an ambient air sample, using gas chromatography. Dissolved gas concentrations in the stream water at time of sampling were calculated using Henry’s law (Hope et al., 1995) and expressed in units of ppmv and $epCO_2$. Environmental variables including soil temperature and depth of water table were provided from a micrometeorological station located ~400 m from the stream sampling point (M. Coyle, personal communication, 2011).

2.2. Sampling of dissolved CO₂ using passive samplers

We deployed passive samplers similar in design to those previously used to sample CO₂ from a range of environments (Garnett and Hardie, 2009; Garnett et al., 2009; Garnett and Hartley, 2010). The samplers were constructed from glass tubing with a central compartment containing Type 13X zeolite molecular sieve (1/16” pellets, BDH, UK) held in place using quartz wool, and surrounded on either side by lengths of narrower glass tubing (Fig. 1). The central compartment was made from glass tubing with dimensions of 70 mm length and 11 mm inner diameter. The ends of the cartridges were built from 100 mm lengths of glass tubing with inner diameters of 4 mm and 8 mm. Lengths (50 mm) of Tygon tubing (Fisher,
UK) were attached to either end of the cartridge, and a plastic clip (WeLoc, Scandinavia Direct, UK) placed over the Tygon tubing at the wider end to create a seal. At the upstream end of the sampler (the narrow end; ‘inlet’) we used a gas permeable hydrophobic filter to allow gas exchange with the inside of the cartridge but prevent the entry of water. The hydrophobic filter was constructed from a 5 cm length of Accurrel PP V8/2 HF tubing (Membrana GmbH, Germany; Gut et al., 1998) pushed onto a 5 cm length of nylon tubing, which was in turn inserted into the Tygon tubing of the inlet of the sampler. A glass stopper was used to seal the end of the Accurrel filter, and joins reinforced using a rubber sealant (Plasti-dip, USA). The resulting samplers were thus completely water-tight, but allowed rapid gas exchange to occur through the hydrophobic filter. This allowed CO2 to enter the cartridge and subsequently be adsorbed onto the molecular sieve. Prior to use, the samplers were prepared by heating (500 °C) the molecular sieve under vacuum (see Hardie et al., 2005) and filled with high-purity N2. Before and after sampling a plastic clip was also placed across the Tygon tubing at the inlet of the sampler to prevent ingress of atmospheric CO2.

For deployment at the field site the sampler was protected inside a length of polystyrene pipe, and attached to a steel ‘cradle’ using cable ties. Posts were driven into the stream banks (to avoid disturbance to the stream bed) to which a length of PVC pipe (110 mm inner diameter x 500 mm length) was secured, such that it was permanently submerged in the water, parallel to stream flow, and located just above the stream bed to allow free flow of water around the passive sampling system. The pipe was used to house the cartridge containing the passive sampler during sampling, ensuring that the sampler was consistently held at the same location and to provide protection from possible damage during high flow periods. Stream water was free to pass unhindered through the pipe which remained open at both ends (Fig. 1).

Prior to sampling, the cradle containing the passive sampler was submerged in the stream, the clip at the inlet removed, and the cradle inserted into the pipe with the inlet of the sampler pointing upstream. The samplers were left for between 27 and 83 days to accumulate CO2,
and then retrieved by first sealing the inlet with a clip before removal from the stream, and
returning to the NERC Radiocarbon Facility for processing. A total of nine samples were
collected over a complete year from 28 May 2010 to 2 June 2011, with a hiatus (14 Dec 2010
to 18 January, 2011) when no sampling occurred. Although the reliability of the passive
samplers had previously been demonstrated on several earlier occasions (Garnett et al., 2009;
Garnett and Hardie, 2009; Garnett and Hartley, 2010), we performed a further test by
deploying an additional second passive sampler simultaneously with the final two from the
annual series; reliability of the samplers would be supported if the isotope concentration of
the CO₂ from the additional sampler was equal to the average of that from the two shorter-
term samplers.

2.3. Measurement of volume of CO₂ recovered and its carbon isotope (δ¹³C and ¹⁴C) content
Sample CO₂ was recovered from the molecular sieve in the passive samplers by heating (500
°C) followed by cryogenic purification (see Hardie et al., 2005). The total volume of CO₂
recovered was measured in a calibrated volume using a pressure transducer, and the CO₂
divided into aliquots for ¹³C and ¹⁴C measurement. δ¹³C (¹³C isotope enrichment relative to
the Vienna PDB standard) was determined using isotope ratio mass spectrometry (VG
Optima, Micromass, UK) at the NERC Radiocarbon Facility. The aliquot of CO₂ for ¹⁴C
analysis was graphitised using Fe/Zn reduction (Slota et al., 1987) and measured by
accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research
Centre (East Kilbride, UK). ¹⁴C concentrations were determined relative to the oxalic acid
international radiocarbon standard and normalised to a δ¹³C of -25 ‰ (using the δ¹³C values
of the recovered CO₂) to account for mass dependent fractionation effects (Stuiver and
Polach, 1977). Radiocarbon results are expressed as %modern and conventional radiocarbon
age (years BP, where 0 BP = AD 1950). By convention measurement uncertainties for isotope
results are expressed as standard deviations (Stuiver and Polach, 1977). Previous tests have
quantified a small isotopic fractionation that occurs during passive trapping (Garnett et al.,
2009; Garnett and Hardie, 2009) and therefore a correction (+4 ‰) was applied when
interpreting the $\delta^{13}$C results; since the $^{14}$C values are by definition normalised to $\delta^{13}$C of -25% they are unaffected by this fractionation effect.

Rate of CO$_2$ trapping on passive samplers should be directly proportional to the CO$_2$ concentration of the environment being sampled as in the following equation based on Fick’s Law (Bertoni et al., 2004):

$$C_i = \frac{(Q_i \times L)}{(S \times t \times D_i)}$$  \hspace{1cm} (1)

where $C_i$ represents the CO$_2$ concentration of the atmosphere being sampled, $Q_i$ the volume of CO$_2$ trapped during time $t$, $D_i$ is the diffusion coefficient of CO$_2$ in air, and $L$ and $S$ are the length and cross-sectional area of the sampling probe (between mid points of inlet and molecular sieve). We used Equation 1 to determine the concentration of dissolved CO$_2$ in the Black Burn during the periods of sample collection, based on the recovered volumes of CO$_2$ from passive samplers and their known exposure times.

3. Results

3.1 Variability in discharge, temperature and CO$_2$ concentrations

Mean discharge from the Black Burn was 54 L s$^{-1}$ and ranged from 3 L s$^{-1}$ to 1400 L s$^{-1}$ over the course of the sampling year (Fig. 2). Due to equipment failure there were two periods when discharge was not recorded. Mean air temperature was 8.0$^\circ$C and ranged from -12.0 to 24.1$^\circ$C (Fig. 2). Concentrations of dissolved CO$_2$ in the stream (Fig. 3) determined from weekly spot sampling ranged from 1301 to 7745 ppmv with a mean of 3570 ppmv. These values represent a range in $epCO_2$ ($ep$ is defined as excess partial pressure e.g. $pCO_2$ water/$pCO_2$ atmosphere) from ~3 to 20.

3.2 Volume and rate of CO$_2$ trapped on passive samplers
The volume of CO$_2$ recovered from the passive samplers (Table 1) ranged from 5.3 ml (27 day and 45 day sampling periods) up to 22.4 ml (83 day sampling period), and was highly positively correlated ($r^2 = 0.788; p < 0.001$) with exposure time. The CO$_2$ trap rate (volume of CO$_2$ recovered divided by number of sampling days) ranged from 0.118 to 0.299 ml day$^{-1}$, with highest rates occurring during summer and lowest during mid-winter, coinciding with the highest and lowest CO$_2$ concentrations, respectively. Using Fick’s law (Equation 1) the estimated average CO$_2$ concentration in the Black Burn, based on the trap rates of the passive sampler, was 3336 ± 229 (SE) ppmv and therefore similar to the mean value derived from spot sampling (3570 ± 225 (SE) ppmv). Throughout the sampling year there was good agreement between the values of dissolved CO$_2$ concentration determined from weekly spot sampling and those calculated from the molecular sieve trap rate (Fig. 3) with an overall significant positive correlation ($r^2 = 0.672, p < 0.01$).

3.3 Carbon isotope ($\delta^{13}$C and $^{14}$C) concentration of dissolved carbon dioxide

All passive samplers provided sufficient CO$_2$ for both $^{14}$C and $\delta^{13}$C measurement. Radiocarbon concentration of the dissolved CO$_2$ ranged from 86.01 to 91.57 %modern (equivalent to 707 to 1210 years BP; Table 1). There was a trend of increasing $^{14}$C concentration in CO$_2$ from the start of the sampling period (May 2010) to peak levels in samples collected between September and December 2010. Subsequently, the $^{14}$C content of dissolved CO$_2$ decreased to that at the start of the time series (Table 1).

Radiocarbon concentration of the dissolved CO$_2$ was compared to mean discharge rates (averaged over the sampling period for each sampler). Due to two gaps in the discharge data, only results for eight of the ten samplers could be reliably compared (Fig. 4). There was a positive correlation between discharge and $^{14}$C concentration of the dissolved CO$_2$ ($r^2 = 0.766, p < 0.01$). However, one sample (collected 9 September 2010 to 6 October 2010) appeared to be an outlier, and when removed the correlation between discharge and $^{14}$C content of CO$_2$ considerably improved ($r^2 = 0.965, p < 0.001$). There was no significant correlation between
the $^{14}$C results and air temperature. In contrast to the $^{14}$C data, $\delta^{13}$C varied relatively little during the course of the sampling year (range -24.2 to -23.0 ‰) and was not significantly correlated with any other measured variables (Table 1).

The means of the $^{14}$C and $\delta^{13}$C values for the two samples collected consecutively between 4 March 2011 to 21 April 2011 and 21 April 2011 to 2 June 2011 were within measurement uncertainty (2 $\sigma$) of the results for the replicate sampler that was exposed during the same sampling period (4 March 2011 to 2 June 2011).

4. Discussion

4.1 Reliability of the passive sampler for collecting dissolved CO$_2$ for $^{14}$C analysis.

Passive samplers have been used reliably to trap CO$_2$ for monitoring purposes, for example to provide time-weighted averages for atmospheric CO$_2$ concentrations (e.g. Bertoni et al., 2004). The sampler used in the present study has previously been shown to perform reliably for sampling and subsequent carbon isotope analysis of CO$_2$ recovered from a range of environments (Garnett et al., 2009; Garnett and Hardie, 2009; Garnett and Hartley, 2010); the many tests performed in these studies included comparison of replicate field samples and verification using isotopic standards under controlled laboratory conditions. Indeed, given that the layers of peatlands beneath the water table have moisture contents of typically > 90 %, the tests performed by Garnett and Hardie (2009) have already shown the reliability of the samplers under similar conditions to this study. We therefore mainly rely on the detailed method testing carried out by Garnett and Hardie (2009) and others (Garnett et al., 2009; Garnett and Hartley, 2010), that have demonstrated the reliability of the samplers. However, the results from the present study also provide additional evidence for the reliability of the passive sampling method for recovering samples of streamwater dissolved CO$_2$ for carbon isotope analysis.
Firstly, the dissolved CO$_2$ concentration determined from the rate of CO$_2$ trapping in passive samplers was remarkably similar to the mean of independently determined values from spot samples (Fig. 3). This is despite the fact that the spot samples were collected at an average frequency of one per week, whereas the passive samplers were sampling continuously. It is possible that the frequency of the spot sampling collection meant that periods of high discharge (Fig. 2) were under-represented, and therefore average CO$_2$ concentration of the spot samples would be slightly biased towards periods of lower flow. Dinsmore and Billett (2008) previously found a strong negative curvilinear relationship between discharge and dissolved CO$_2$ concentration ~ 20 m downstream of the current study site (using in-situ CO$_2$ sensors with 30 min time resolution). This could explain why a slightly lower annual average for CO$_2$ concentration was calculated using the passive samplers compared to the spot sampling approach. Indeed, discharge during the sampling year on the days when spot samples were collected was on average 50.28 L s$^{-1}$, compared to 53.98 L s$^{-1}$ from the continuous logger; thus over the sampling year the mean discharge was 7.37 % greater than when spot samples were collected. If we decrease the mean CO$_2$ concentration for the spot samples by the same percentage difference to account for the spot sampling bias to low flows (i.e. assuming a negative linear relationship over this small range), the CO$_2$ concentration of the spot samples becomes 3307 ppm, remarkably similar to the CO$_2$ concentration calculated from the passive samplers (3336 ppm). The strong correlation between the CO$_2$ concentrations derived from spot samples compared to passive samplers shows that the rate of CO$_2$ trapping was related to the CO$_2$ concentration of the environment being sampled. This is fundamentally important for the collection of representative samples. The rate of CO$_2$ trapping in the samplers appears to have been unaffected by the length of exposure time, since the latter varied considerably (from 27 to 83 days) throughout the sampling year. This indicates that the sampling capacity of the passive samplers was not exceeded (Garnett et al. (2009) found that the capacity of the sieves was at least 100 ml CO$_2$). It should however be noted that in the replicated samples at the end of the
annual series, that the summed volume (19.7 ml) recovered from the two short-period samples (4 March to 21 April 2011, and 21 April to 2 June 2011) was slightly less than the volume (22.4 ml) recovered from the single sampler that was exposed for the entire period (4 March to 2 June 2011). Previous tests of the passive sampler have generally shown closer agreement in the volumes of CO2 recovered from replicate samplers (e.g. Garnett et al., 2009). Clearly, we can discount the possibility that the longer-term sampler was trapping CO2 less efficiently due to it becoming saturated with either CO2 or H2O, since this sampler had the greater CO2 volume. While we aimed to place replicate samplers as close to each other as possible in the stream, there may have been slight differences in the concentration of CO2 at the locations where these samplers were deployed (using Equation 1 we calculate that a difference of ~ 460 ppm (i.e. < 14 %) in streamwater CO2 concentration would explain the different volumes recovered). Alternatively, part of the discrepancy could be due to small differences in the dimensions of passive samplers, for example, a difference in the distance between the gas inlet and molecular sieve of just 1 cm would have resulted in a difference in the volume of CO2 trapped in the 83 day sample of ~ 1 ml. Clearly, if the passive samplers are to be used to more accurately quantify CO2 concentrations in streamwater further investigation of this discrepancy is required. However, it should be reiterated that the main purpose of this study was to measure $\delta^{13}$C and $^{14}$C and not CO2 concentration, and that these were unaffected by the above mentioned issues. It is also important to note that when carbon isotope values for these replicate samples were combined, both the $^{13}$C and $^{14}$C values from the short period samplers were within measurement uncertainty (2 $\sigma$) of the results for the long period sample, supporting the earlier studies that demonstrated the reliability of the samplers for isotopic determinations.

4.2 Carbon isotope ($^{14}$C and $\delta^{13}$C) composition of dissolved CO2.

We found very little variation in the $\delta^{13}$C of streamwater dissolved CO2 collected in the passive samplers over the course of the sampling year, and no clear temporal pattern or significant correlations with variables such as flow or temperature. After correction of the
results for fractionation during passive trapping (see Methods), $\delta^{13}C$ ranged from -20.2 to -19.0‰. This range of values is similar to earlier measurements of evaded CO$_2$ from the Black Burn collected using a floating chamber; Billett et al. (2006) reported values of ~-21.6 to -21.0‰ and Billett et al. (2007) values of -26.5 to -18.3‰. The lack of a clear pattern in the annual series or correlations with other variables means that alone, the series of $\delta^{13}C$ values is of limited use in unravelling the carbon dynamics at this site, other than to say that the values themselves could result from a mixture of sources, including dissolved CO$_2$ from shallow or deep peat, and with potentially a small contribution from a weathering source. The lack of variation in the values over the 12 month period may suggest that hydrological flow paths within the catchment are delivering CO$_2$ to the stream from a source area/areas with a consistent $\delta^{13}C$ value. Alternatively, the results may partly reflect the time-integrated sampling method, which in some situations could be a disadvantage of the technique.

Although our results clearly indicate that no seasonal pattern in $\delta^{13}C$ existed, we cannot rule out the possibility that significant variability such as that observed by Billett et al. (2007) exists across shorter time scales i.e. at a diurnal level or in response to short term storm events. But as long as prior consideration is given to the scale of variability being targeted, and the length of time over which integration occurs is adjusted to suit, the smoothing which occurs due to time integration is not necessarily a disadvantage.

In contrast, the $^{14}C$ values of dissolved CO$_2$ collected from this peatland stream using the passive samplers showed a clear pattern over the course of the year and were strongly correlated with stream discharge (Fig. 4). The $^{14}C$ age of the dissolved CO$_2$ ranged from 1210 to 707 years BP, and again was similar to the age of evaded CO$_2$ collected from the Black Burn in previous studies. For example, Billett et al. (2006) reported $^{14}C$ ages of 1454 to 852 years BP for samples collected at two locations along the Black Burn on the same day, and Billett et al. (2007) gave an age range from 1127 years BP to modern (104.58 %modern) for samples collected at two sites along the Black Burn on four seasonal sampling occasions; of these two sites, the one nearest our sampling point had a range of $^{14}C$ ages of 312 to 1127...
years BP. These results broadly imply that the age of CO₂ evaded at this site differs little from
the streamwater dissolved CO₂; this concurs with the results of Billett and Garnett (2010) who
for the same site found similar ¹⁴C values for evaded CO₂ and dissolved CO₂ (derived from
¹⁴C analysis of total streamwater DIC) when samples were collected concurrently (e.g. for site
A10 on two separate occasions, evasion/DIC were respectively, 759/714 years BP, and
940/890 years BP).

The series of ¹⁴C measurements of dissolved CO₂ shows a general pattern of increasing ¹⁴C
concentrations from May, to greatest ¹⁴C-enrichment in the September samples, followed by a
progressive decline and return to the lowest ¹⁴C levels the following May (Fig. 4). The ¹⁴C
values imply that the dissolved CO₂ in streamwater contains a greater proportion of younger
carbon in autumn and early winter, compared to the rest of the year. An obvious source for
younger carbon in peatlands is vegetation; CO₂ with a contemporary ¹⁴C signal (~104.5
%modern at the time of this study; Levin et al., 2008) is fixed through photosynthesis and
released into the soil via plant respiration, root exudates or litter decomposition. However, it
seems unlikely that plant activity or CO₂ mineralised from recently deposited plant litter or
surface peat can explain the pattern of ¹⁴CO₂ in the streamwater in the annual series, since we
would expect greatest plant activity and/or greatest decay of fresh litter/surface peat during
the summer season when temperatures were highest; in fact the ¹⁴C results suggest greatest
contributions from younger carbon much later (September-December). There could be a time
delay between CO₂ production and transfer to the stream as has been reported for DOC in
peatland sites (Clark et al., 2005; Dawson et al. 2011). Regression analysis of CO₂
concentrations in soils and associated surface waters have found that introducing lag times of
<1 day to 14 days improved the modelling of CO₂ cycling in aquatic systems (Hope et al.
2004; Dinsmore et al. 2009b). However, to explain the pattern of our ¹⁴CO₂ results the time
delay would need to be much greater than this (and greater than the 4-6 weeks reported for
DOC). It further seems unlikely that a simple time delay can explain the pattern of ¹⁴CO₂
because there was no significant correlation between mean air temperature and %modern of
dissolved CO2 (which would be expected to correlate even with a time delay).

Instead, a strong correlation was observed between the $^{14}$C content of the dissolved CO2 and stream discharge, such that there was a greater proportion of younger carbon in the dissolved CO2 during sampling periods when discharge was greatest (Fig. 4). Previous studies have shown using supporting geochemical measurements (e.g. Ca concentrations; Tipping et al., 2010) that streams draining peats can contain a significant groundwater signature. Given that groundwater that has passed through carbonate geology is likely to contain some ancient ($^{14}$C-dead) dissolved CO2, an explanation for the correlation between the $^{14}$C content of streamwater dissolved CO2 and discharge in our results, could be a change in the proportion of groundwater-derived CO2. Thin limestone bands, within a dominantly sandstone-shale sequence are known to occur beneath the peat and fluvial-drift in the Auchencorth Moss catchment (Dinsmore et al., 2010) and are a potential source of groundwater-derived CO2 to the stream system. If for example, streamwater had a constant groundwater component, but changes in discharge resulted from the incorporation of different levels of surface runoff or water from the surface layers of peat, then we would expect to find a positive correlation between discharge and the $^{14}$C content of the dissolved CO2. This is similar to what we have observed. However, given the known extremes in the $\delta^{13}$C values between a geological CO2 source (~0 ‰) and an organic-derived (C3 plants) source (~ -30 to -25 ‰), we would expect based on mass balance to also find a correlation between streamwater $\delta^{13}$C and discharge. The fact that we do not see this relationship, and if anything, $\delta^{13}$C becomes more enriched at higher flows (converse to what would be expected), suggests that the pattern in $^{14}$C of dissolved CO2 is not a result of differences in the proportion of groundwater-derived CO2. We do not preclude a groundwater contribution to the streamwater at our site, but suggest that other processes are more likely to be responsible for the observed annual pattern in the $^{14}$C content of dissolved CO2.
It is well known that intact peatlands generally exhibit decreasing $^{14}$C-enrichment in the peat profile with depth which reflects the increasing age of deeper peat (e.g. Clymo and Bryant, 2008). Studies have shown that in these peat profiles, large volumes of CO$_2$ exist in horizons particularly below the water table, which usually refers to depths greater than 10-30 cm. Clymo and Bryant (2008) and others (Charman et al., 1999; Garnett and Hardie, 2009; Billett et al. in press b) have shown that the dissolved CO$_2$ in peat profiles also increases in age with depth (although is typically younger than the surrounding peat). Studies of peatland hydrology have also shown that in periods of high precipitation and/or low evapo-transpiration, water tables are usually within a few centimetres of the peat surface, but that during relative droughts can fall considerably. At the meteorological station on Auchencorth Moss ~ 400 m from our passive sampling site, average water table depth during the sampling year was 5 cm, and fell to a maximum depth of 37 cm in July 2010. Clymo and Bryant (2008) note that the hydraulic conductivity of peats is generally higher at the surface and declines with depth. Thus, during periods when discharge in streams draining peats is highest, it is likely that the water table across the catchment will be close to the peat surface, and since hydraulic conductivity is greatest in the surface peat, it is reasonable to expect that a proportionally greater amount of the stream discharge is represented by water that has passed through the surface layers. In contrast, during periods of relative drought, stream discharge is lower and water tables are set relatively deeper in the peat profile. Assuming that peatland water acquires CO$_2$ with a $^{14}$C signature that reflects the depths in which it has moved through, then we would expect that during periods of high stream flow that the streamwater would contain a proportionally greater amount of water from nearer the peat surface or from overland flow. Since CO$_2$ derived from the peat surface will be relatively $^{14}$C-enriched (and younger), we would expect a positive relationship between discharge and the $^{14}$C content of streamwater dissolved CO$_2$, which we found.

Although the above interpretation explains the observed positive correlation between $^{14}$C concentration in the dissolved CO$_2$ and stream discharge, we found $\delta^{13}$CO$_2$ was unrelated to
annual changes in stream discharge. Clymo and Bryant (2008), Steinmann et al. (2008) and Garnett and Hardie (2009) have all shown that $\delta^{13}C$ of dissolved CO$_2$ in peat profiles varies considerably, with a trend of increasing $^{13}C$-enrichment with depth as a consequence of anaerobic decomposition. However, since the zone of water table fluctuation at this site and others (e.g. Tipping et al., 2010) is typically restricted to only a few 10’s of centimetres in the surface layers of the peat profile, the depth-related changes in $\delta^{13}CO_2$ in the peat water are unlikely to be more than a few per mil. Therefore, we would not expect to observe a correlation between $\delta^{13}C$ of streamwater-dissolved CO$_2$ and discharge.

Studies (e.g. Clymo and Bryant, 2008; Steinmann et al., 2008; Garnett and Hardie, 2009) have also shown that the concentration of dissolved CO$_2$ in peats increases with depth. Therefore, if deeper layers are responsible for contributing proportionally more CO$_2$ to stream flow during periods of low discharge, we would also expect that the CO$_2$ concentration in the streamwater would be higher in periods of low flow. We indeed found this to be the case, with a strong negative correlation observed between discharge and CO$_2$ concentration in streamwater (Fig. 5); Dinsmore and Billett (2008) have previously reported a similar negative CO$_2$ concentration-discharge relationship for the study stream, Black Burn.

If linear regression is applied to the stream discharge and $^{14}$CO$_2$ results we obtain the equation $y = 0.0607x + 85.607$ ($r^2 = 0.766$, $p < 0.01$), where $y = ^{14}$C %modern and $x$ = discharge (Fig. 6). Therefore, the intercept shows that when discharge is zero, the $^{14}$C content of the dissolved CO$_2$ is 85.6 %modern (equivalent to ~ 1250 years BP). This may imply that there is a baseline source of CO$_2$ to the stream, representing the age of the CO$_2$ that enters the stream when contributions from younger surface layers are insignificant. At two other Scottish sites, CO$_2$ of approximately this age was found to occupy depths in the peat profile of 1 m (Garnett and Hardie, 2009) and 2 m (Clymo and Bryant, 2008), which may imply that much of the baseline flow of the Black Burn is derived from similar depths. However, water table depth at Auchencorth Moss only fell to a maximum depth of 37 cm below the surface during the
sampling year, a depth where presumably CO$_2$ dissolved in the peat water would be much younger; this therefore suggests that even under baseflow conditions streamwater dissolved CO$_2$ is likely to be derived from a range of depths (but with an average age of ~ 1250 years BP). The $^{14}$C content of the dissolved CO$_2$ under baseflow conditions implied from the intercept also indicates that geological sources cannot represent a major component of the streamwater dissolved CO$_2$ (otherwise we would have expected the $^{14}$C content of dissolved CO$_2$ to be closer to 0 %modern). This is in contrast to the suggestion by Billett et al. (2007) that weathering of carbonate may provide a significant contribution to dissolved CO$_2$ to the Black Burn.

It was notable that the correlation between stream discharge and $^{14}$C content of dissolved CO$_2$ improved considerably after the removal of an outlier. While it would be wrong to draw substantial interpretations from a single data-point, it is perhaps worth commenting that for the sample collected between September to October the $^{14}$C content of the dissolved CO$_2$ was considerably higher than expected based on the discharge values. Net ecosystem exchange measurements made using an eddy covariance system within the catchment show a strong seasonal cycle in vegetation productivity (Billett et al., 2004). The $^{14}$C outlier identified could therefore represent a flush of young carbon being released into the drainage water at the end of the growth period and perhaps merits further investigation.

5. Conclusions

The present study has demonstrated the value of a new passive sampling method for the collection of dissolved CO$_2$ from streamwater. Our results support earlier tests used to validate and apply the method in the field environment (Garnett et al., 2009; Garnett and Hardie, 2009; Garnett and Hartley, 2010). A clear benefit of the method is that the recovered sample is composed of CO$_2$ collected continuously throughout the sampling period, and therefore is not vulnerable to under-sampling short-term events such as floods, when most dissolved CO$_2$ is transported at these sites (Dinsmore and Billett, 2008). While we chose to
deploy the method to investigate the time-series of dissolved CO$_2$ in our study, the simplicity of the technique and minimal infrastructure requirements (e.g. it requires no external power) means that it could also be conveniently used, for example, to investigate changes in the isotopic composition of dissolved CO$_2$ as it is transported from headwater source to sea (e.g. Dawson et al., 2009).

The $\delta^{13}$C value of streamwater dissolved CO$_2$ collected using the passive samplers varied only slightly over the study year, indicating relatively little change in the source of the CO$_2$. $^{14}$C analysis of the CO$_2$ confirmed the results of earlier studies at the site and demonstrated the release of old CO$_2$ from this peatland stream. Unlike the $\delta^{13}$C results, the $^{14}$C values for dissolved CO$_2$ showed a clear seasonal pattern, with the oldest CO$_2$ being transported by the stream in spring/early summer. Based on the above observations, and a positive correlation between the $^{14}$C age of dissolved CO$_2$ and discharge, we conclude that although total CO$_2$ in this peatland stream is likely derived from a range of peat depths, shallower/younger peat layers contribute greater amounts of CO$_2$ during periods of high discharge, as a result of a greater proportion of streamwater having passed through shallower peat. The method clearly has the potential to make a significant contribution to our understanding of CO$_2$ sources and transport processes in a range of different soil-stream systems.

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References


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Figure Captions

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

Fig. 2 Discharge from the Black Burn and air temperature (measured ~ 400 m from the stream sampling point) over the course of the sampling year from May 2010 to June 2011.

Fig. 3 Concentration of dissolved CO$_2$ in the Black Burn from May 2010 to June 2011 determined by i) continuous trapping using passive samplers and ii) spot sampling of stream water. CO$_2$ concentration determined for the passive samplers based on the CO$_2$ trap rate and Fick’s law (see text). Mean, min and max values for spot samples reflect the sampling periods of the associated passively collected sample.

Fig. 4 Mean discharge (± SE) of the Black Burn and $^{14}$C content of dissolved CO$_2$ (± 1σ) over the sampling year from May 2010 to June 2011, showing increased $^{14}$C content of CO$_2$ at times of greater discharge. Using all data points resulted in a positive correlation ($r^2 = 0.766; p < 0.01; n = 8$) which improved considerably when the September 2010 sample was omitted ($r^2 = 0.965; p < 0.001; n = 7$).

Fig. 5 Mean discharge of the Black Burn and CO$_2$ concentration determined from spot samples (± SE). Mean values for both discharge and CO$_2$ concentration reflect the sampling periods of the associated passively collected sample. There was a strong negative correlation between discharge and CO$_2$ concentration ($r^2 = 0.855; p < 0.001; n=8$; note 2nd y-axis is reversed).
Fig. 6 Radiocarbon concentration of dissolved CO$_2$ (± 1 σ) versus mean discharge (± SE) of the Blackburn for samples collected over the sampling year from May 2010 to June 2011. Mean values for discharge reflect the sampling periods of the associated passively collected $^{14}$CO$_2$ sample.
Molecular sieve held in place by quartz wool

Glass tubing

Tygon tubing with removable clip to seal

Accurel PP v8/2 HF tubing

Polystyrene pipe and steel cradle for field deployment

Section of drainpipe secured to stream bed

Handle larger than width of drainpipe to hold in place

Molecular sieve held in place by quartz wool

Water flow direction
Fig. 3

![Graph showing CO2 concentration over time]

- Passive samplers
- Spot samples (mean)
- Spot samples (min/max)

Mid-point of sampling period

CO2 concentration (ppmv)

1 May 2010 to 5 Jun 2011
Fig. 5

Discharge (L s$^{-1}$)

Mid-point of sampling period

Discharge

CO$_2$ concentration
Fig. 6

\[ y = 0.0607x + 85.607 \]

\[ r^2 = 0.7661 \]

\[ p < 0.01 \]