

## A DIRECT METHOD TO MEASURE $^{14}\text{CO}_2$ LOST BY EVASION FROM SURFACE WATERS

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**ABSTRACT.** Recent methodological advances in the use of zeolite molecular sieves for measuring the isotopic signature of  $\text{CO}_2$  have provided the opportunity to make direct measurements of  $^{14}\text{CO}_2$  in various field situations. We linked a portable molecular sieve/pump/IRGA system to a floating chamber to demonstrate the potential of the method to quantify the isotopic signature ( $\delta^{13}\text{C}$  and  $^{14}\text{C}$ ) of  $\text{CO}_2$  lost by evasion (outgassing) from surface waters. The system, which was tested on a peatland stream in Scotland, involved 1) an initial period of scrubbing ambient  $\text{CO}_2$  from the chamber, 2) a period of  $\text{CO}_2$  build-up caused by surface water evasion, and 3) a final period of  $\text{CO}_2$  collection by the molecular sieve cartridge. The field test at 2 different sites on the same drainage system suggested that the results were reproducible in terms of  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  values. These represent the first direct measurements of the isotopic signature of  $\text{CO}_2$  lost by evasion from water surfaces.

### INTRODUCTION

Surface waters in parts of the world are potentially significant flux pathways for  $\text{CO}_2$  transport to the atmosphere; this has raised interesting questions about the nature and origin of  $\text{CO}_2$  in terrestrial aquatic systems. In the Amazon Basin, evasion of  $\text{CO}_2$  from wetlands is thought to account for  $0.5 \text{ Gt C yr}^{-1}$  and may represent a significant proportion of the “missing” C in the global carbon cycle (Richey et al. 2002). Recent isotopic data have confirmed that the  $\text{CO}_2$  is mainly derived from respiration of young (<5 yr) allochthonous organic matter (Mayorga et al. 2005); this highlights the important role that isotopes can play in establishing key terrestrial C pathways (Grace and Malhi 2002). Streams and lakes associated with northern peatlands are also typically supersaturated with  $\text{CO}_2$  (Kling et al. 1991), which is almost wholly lost to the atmosphere by evasion. Initial measurements at 2 Scottish peatland sites (Hope et al. 2001; Billett et al. 2004) suggests that the flux is significant and may be comparable to other flux terms in the peatland C cycle.

The ease of collecting streamwater dissolved and particulate organic carbon (DOC and POC) samples coupled with the use of accelerator mass spectrometry (AMS) means that natural abundance  $^{14}\text{C}$  data are providing a significant amount of information about the age of organic carbon in surface waters. These data suggest that most, but not all, DOC in streamwater is modern (post-bomb,  $^{14}\text{C}$ -enriched) carbon (Schiff et al. 1997; Raymond and Bauer 2001a,b; Palmer et al. 2001). Older DOC with depleted  $^{14}\text{C}$  values appear to be derived from catchments like the Hudson River characterized by a higher degree of disturbance of the soil C pool (Raymond and Bauer 2001a). Data for rivers draining into the North Atlantic suggest that POC is  $^{14}\text{C}$ -depleted, with  $^{14}\text{C}$  ages ranging from modern to 4763 BP (Raymond and Bauer 2001a).

In contrast to DOC and POC and with the exception of the work by Mayorga et al. (2005), relatively little is known about the origin of  $\text{CO}_2$  in streams and rivers. Methodological constraints have restricted isotopic studies of streamwater  $\text{CO}_2$ , which have been based on an acidification step that converts all the dissolved inorganic carbon (DIC) to  $\text{CO}_2$ , which is then captured cryogenically. This indirect “gas stripping” method, based on a procedure developed for seawater (Kroopnick et al. 1970; Kroopnick 1974), has been used to study the  $^{13}\text{C}$  composition of DIC in freshwaters and large river estuaries (Quay et al. 1992; Pawellek and Veizer 1994; Yang et al. 1996; Atekwana and Krishnamurthy 1998; Palmer et al. 2001). It has also been used to study  $^{14}\text{CO}_2$  evolution from  $^{14}\text{C}$  labeled

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organic substrates (e.g. Taylor et al. 1981). A recent paper by Mayorga et al. (2005), which presents  $^{14}\text{C}$  and  $^{13}\text{C}$  isotopic composition data for  $\text{CO}_2$ , is based on IRMS and AMS analysis of cryogenically purified  $\text{CO}_2$  stripped after acidification of preserved water samples. The main difficulty with this indirect “gas stripping” method is that the isotopic composition of  $\text{CO}_2$  lost by evasion is calculated and makes a number of assumptions about equilibrium reactions involving the various forms of DIC in streamwater ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , free  $\text{CO}_2$ ). The composition of DIC in freshwater is strongly pH dependent and is derived from a variety of sources, such as weathering, in-stream respiration of organic matter, soil inputs of  $\text{CO}_2$ , and atmospheric invasion of  $\text{CO}_2$  (Wetzel 1983). There is a need to develop a direct method, which does not involve chemical manipulation of water samples, to both age and source the origin of  $\text{CO}_2$  lost by evasion from water surfaces.

The method presented here uses a combination of a floating chamber and zeolite molecular sieves to trap sufficient  $\text{CO}_2$  for AMS analysis. Molecular sieves have been used successfully to trap  $\text{CO}_2$  (e.g. Bauer et al. 1992; Bol and Harkness 1995), and the method described below is based on a system designed and tested for portable use in the field (Hardie et al. 2005). The method was tested at 2 sites on Black Burn, a peatland stream draining Auchencorth Moss, located 17 km SW of Edinburgh (central Scotland). The catchment (335 ha) is the site of a major study of evasion from surface waters and is characterized at its outlet by low pH (mean 4.7), high TOC (mean  $40.7 \text{ mg L}^{-1}$ ) drainage waters (Billett et al. 2004).

## METHODS

Samples for the isotopic determination of  $\text{CO}_2$  lost by evasion from surface waters were collected by linking a portable zeolite molecular sieve/pump/IRGA (infrared gas analyzer) system (Hardie et al. 2005) with a floating chamber (Figure 1). The latter consists of a 1-kg brown opaque injection molded polypropylene box supplied by H C Slingsby plc (UK), external dimensions 30.5 cm (length), 30.5 cm (width), and 15.2 cm (height). The base of the box (volume:  $9464 \text{ cm}^3$ ; basal area:  $728 \text{ cm}^2$ ) has a 1-cm-wide lip, making it both stable and easier to form an effective seal with the water surface. Four holes were drilled into “spines” at the corners of the box to enable it where necessary to be held in position at a specific location on the water surface. The sealed chamber has sufficient volume to float freely without any buoyancy aid. To maintain the seal between the chamber and the water surface, the base of the chamber is submerged 2–3 cm below the water level; this decreases the “effective volume” of the floating chamber to  $\sim 9000 \text{ cm}^3$ . Two auto-shutoff Quick Couplings™ (Colder Products Company, USA) were fitted into holes drilled 10 cm from the opposite corners of the upper chamber surface to allow gas to be pumped in and out of the floating chamber.

Subsequent to the use of the above floating chamber, we have found that in higher flow and windier conditions (greater water turbulence) a more stable chamber is necessary to maintain an effective seal with the water surface. We have been successfully using a chamber (supplied by H C Slingsby plc) with a rectangular (rather than square) base with the following external dimensions: 45.5 cm (length), 30.5 cm (width), and 15.2 cm (height). The chamber has a volume of  $15,400 \text{ cm}^3$  and a basal area of  $1141 \text{ cm}^2$ .

Gas transfer between the stream surface and the atmosphere is controlled by the difference in gas concentration and turbulence at the air-water interface (Liss and Slater 1974); the latter caused by factors such as wind shear or, more importantly, streambed roughness and gradient. Locating the floating chamber close to zones of natural (or man-made) turbulence will selectively sample areas of the stream surface with high rates of degassing, and increase the amount of  $\text{CO}_2$  available for trapping by the molecular sieve.

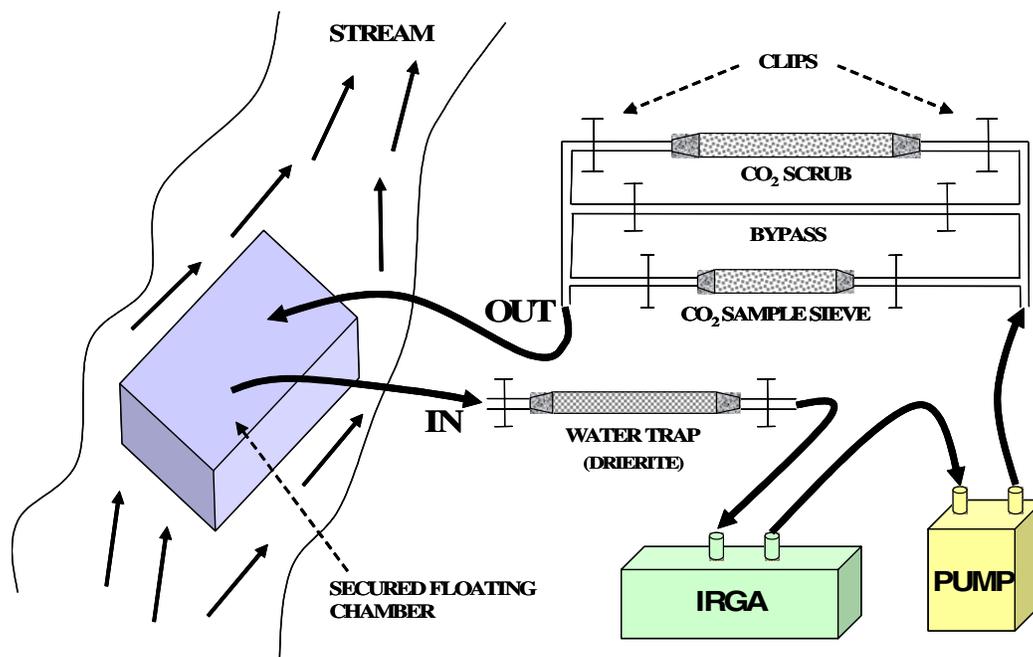


Figure 1 Schematic diagram to show the attachment of the floating chamber with the molecular sieve sampling system in the field.

The floating chamber is connected to a closed-loop sampling system, which first scrubs atmospheric CO<sub>2</sub> from the chamber, allows it to build up in the chamber, and then traps CO<sub>2</sub> lost by evasion from the water surface using a zeolite molecular sieve cartridge containing a type 13X molecular sieve (BDH, UK) (Figure 1). Initially, air from the chamber is drawn through a water trap (drierite; Alfa Aesar, Germany) into a portable IRGA (PP Systems, UK) and then out via a lightweight pump (flow rate  $\sim 600 \text{ mL min}^{-1}$ ) through a soda lime CO<sub>2</sub> scrub cartridge before re-entering the floating chamber through the second auto-shutoff coupling. A series of *T* pieces and WeLoc<sup>®</sup> clips (Scandinavia Direct, UK) allow the CO<sub>2</sub> scrub to be isolated after 30 min during which time 2 chamber volumes of air (18 L) have circulated through the system. CO<sub>2</sub> is then allowed to build up in the chamber as the air passes through an inert bypass cartridge; the rate of build-up can be continuously monitored by the inline IRGA. After a sufficient period of CO<sub>2</sub> build-up in the chamber (a function of the evasion rate), the zeolite molecular sieve cartridge is switched inline and the CO<sub>2</sub> trapped. The sampling time is a function of the rate of CO<sub>2</sub> build-up inside the chamber.

To test reproducibility and CO<sub>2</sub> recovery rates, the whole system was field tested on 13 August 2004 at Black Burn. Duplicate samples were collected from 2 sites (5 and 5A) located 750 m apart on the main stream channel (Figure 2). Evasion rates have been measured on 3 occasions at 5 different points along the main stream channel between January–August 2005 as part of a wider program of measurements in UK peatland streams. These results are presented to show how the  $^{13}\text{C}/^{14}\text{C}$  “test” sites fit into the overall downstream spatial patterns in CO<sub>2</sub> evasion rates along Black Burn.

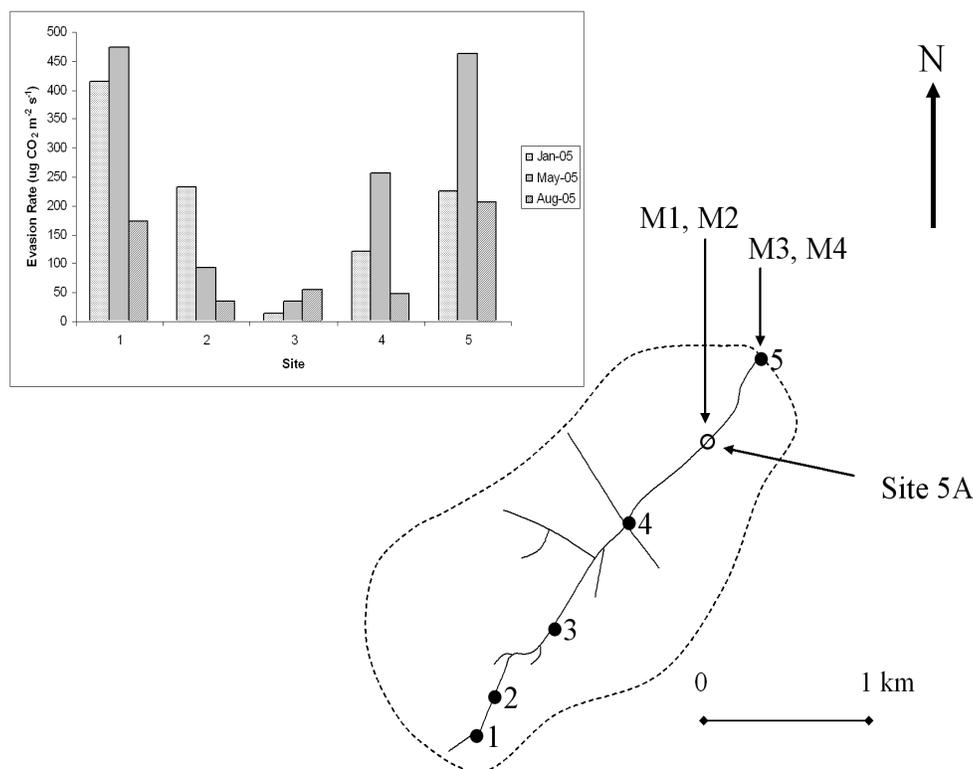


Figure 2 Location of the 2 sampling sites (5 and 5A) within the Auchencorth catchment and the variation in evasion rates along the length of Black Burn.

## RESULTS

Evasion rates on the main stream channel at Auchencorth Moss varied from 14 to  $475 \mu\text{g CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ , with the lowest values occurring in the central part of the catchment where the stream is deep and slow flowing (Figure 2). Downstream trends exhibit significant and consistent spatial variation on different sampling occasions, temporal variation being strongly related to stream flow.

Figure 3 illustrates the changes in CO<sub>2</sub> concentrations occurring during the collection of the 4 “test” samples and demonstrates the 3 stages in the procedure: scrubbing, CO<sub>2</sub> build-up, and sampling. At both sites, CO<sub>2</sub> was scrubbed from the system for 30 min, sufficient time to allow 2 chamber volumes to be circulated through the system. At Site 5A, scrubbing was related to an increase in CO<sub>2</sub> concentrations because CO<sub>2</sub> was evaded from the stream surface faster than it was removed by the soda lime trap. At Site 5, CO<sub>2</sub> concentrations decreased because the evasion rate was lower. Following scrubbing, the rate of CO<sub>2</sub> increase can be used to calculate the evasion rate (knowing the chamber volume and surface area). This was significantly higher at Site 5A (Table 1), with chamber CO<sub>2</sub> concentrations reaching 1055 and 1155 ppmv within 10 min after the start of the build-up period.

We aimed to trap  $\sim 10 \text{ mL}$  of CO<sub>2</sub> for each sample to provide sufficient material for AMS <sup>14</sup>C analysis, <sup>13</sup>C measurement, and to archive a sub-sample. Since previous tests have shown that the molecular sieve cartridges strip all the CO<sub>2</sub> from the airstream (Hardie et al. 2005), the amount of time to collect the required CO<sub>2</sub> was determined from the pump rate and chamber CO<sub>2</sub> concentration. For example, in the case of sample M1, the CO<sub>2</sub> concentration after CO<sub>2</sub> build-up was  $\sim 1000 \text{ ppmv}$ ;

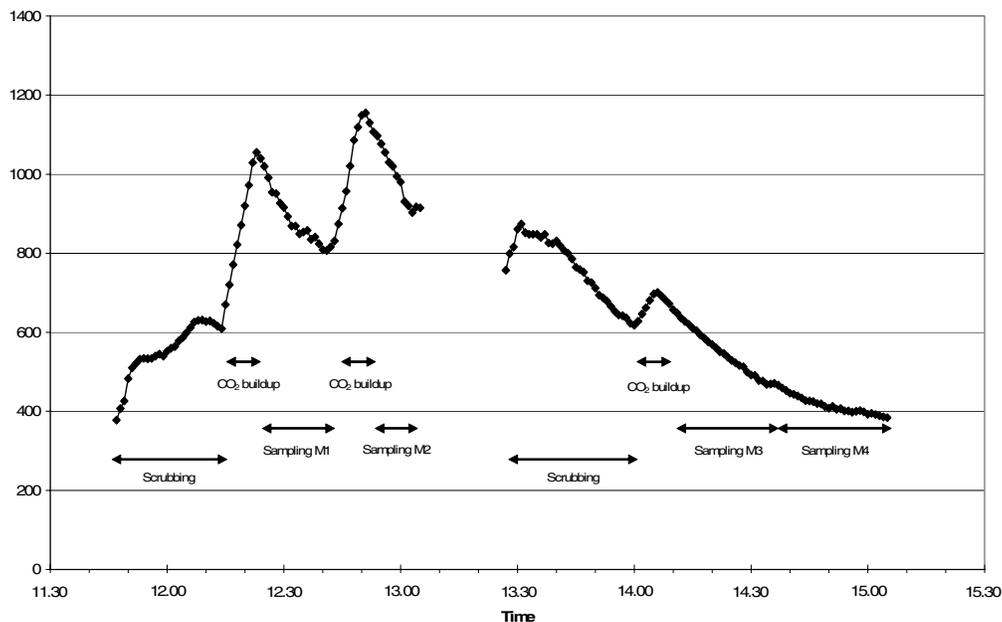


Figure 3 Temporal changes in  $\text{CO}_2$  concentration during scrubbing, build-up, and sampling of  $\text{CO}_2$  during the testing of the method.

Table 1 Isotopic data and evasion rates at the 2 test sites.

Lab code (SUERC-)	Sample identifier	Site	$^{14}\text{C}$ enrichment (% Modern $\pm 1 \sigma$ )	Conventional $^{14}\text{C}$ age (yr BP $\pm 1 \sigma$ )	$\delta^{13}\text{C}_{\text{VPDB}}\text{‰}$ ( $\pm 0.1$ )	$\text{CO}_2$ recovered (mL)	$\text{CO}_2$ evasion rate ( $\mu\text{g CO}_2 \text{ m}^{-2}\text{s}^{-1}$ )
5930	M1	5A	$83.44 \pm 0.30$	$1454 \pm 29$	-21.0	9.9	203
5933	M2	5A	$83.56 \pm 0.30$	$1443 \pm 29$	-21.1	8.6	147
5934	M3	5	$89.94 \pm 0.29$	$852 \pm 26$	-21.0	8.2	60
5937	M4	5	$88.76 \pm 0.29$	$958 \pm 26$	-21.6	6.5	nd

therefore, at a pump rate of  $\sim 600 \text{ mL min}^{-1}$ , approximately  $0.6 \text{ mL min}^{-1}$   $\text{CO}_2$  would be sampled, and so the total required sampling time was  $\sim 17$  min. However, due to  $\text{CO}_2$  trapping on the molecular sieve, the  $\text{CO}_2$  concentration in the chamber progressively decreased (Figure 3) and a slightly longer sampling time was required; for sample M1 we collected a total of 9.9 mL  $\text{CO}_2$  in 18 min. The higher chamber  $\text{CO}_2$  concentration for sample M2 permitted a shorter sampling time (12 min), but since the evasion rates were lower at Site 5,  $\text{CO}_2$  collection in cartridges M3 and M4 took longer (30 min on both occasions).

The molecular sieve cartridges containing the sample require no special storage and were returned to the NERC Radiocarbon Laboratory for processing. The  $\text{CO}_2$  was collected from each sieve cartridge by heating ( $500^\circ\text{C}$ ) and cryogenically collecting the  $\text{CO}_2$  released on a purpose-built vacuum rig (full details of the method are provided by Hardie et al. 2005). A sub-sample of the  $\text{CO}_2$  was graphitized using Fe-Zn reduction and underwent  $^{14}\text{C}$  measurement on the 5MV AMS at the Scottish Universities Environmental Research Centre (Xu et al. 2004). A further sub-sample was analyzed for  $^{13}\text{C}$  concentration using the NERC Radiocarbon Laboratory's IRMS (VG Optima, UK).

$^{13}\text{C}$  concentrations are reported using the delta notation with  $^{13}\text{C}/^{12}\text{C}$  variations relative to the international standard Vienna Pee Dee Belemnite (VPDB), described by the following equation:

$$\delta^{13}\text{C} (\text{‰}) = (^{13}\text{C}/^{12}\text{C})_{\text{Sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{VPDB}} \times 1000(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}$$

$^{14}\text{C}$  results were expressed as ‰ Modern and conventional  $^{14}\text{C}$  age, having been normalized to a  $\delta^{13}\text{C}$  of  $-25\text{‰}$  (Stuiver and Polach 1977).

Table 1 shows that between 6.5 and 9.9 mL of  $\text{CO}_2$  was recovered from the molecular sieve cartridges for the 4 test samples. The replicate samples from Site 5A (M1 and M2) had identical ( $<1 \sigma$ )  $^{14}\text{C}$  ages and  $^{13}\text{C}$  concentrations; however, there was a slight difference between the replicates (M3 and M4) from Site 5. The  $2\text{-}\sigma$  ranges for both the  $^{14}\text{C}$  and  $^{13}\text{C}$  values just failed to overlap. The  $^{14}\text{C}$  age of the evaded  $\text{CO}_2$  differed far more between the 2 sampling locations; the mean age for samples from Site 5A was  $\sim 1450$  BP, whereas 750 m downstream at Site 5 the age of the  $\text{CO}_2$  was 500 to 600 yr younger.

## DISCUSSION AND CONCLUSIONS

While floating chambers have been extensively used to measure gas release rates from lakes, estuaries, rivers, and streams (e.g. MacIntyre et al. 1995; Richey et al. 2002; Borges et al. 2004), the recent development and testing of a portable field system using zeolite molecular sieve cartridges (Hardie et al. 2005) has provided the opportunity to make a methodological step in the isotopic analysis of  $\text{CO}_2$  lost by evasion from water surfaces. This avoids the need for sample acidification and can be carried out entirely in the field. The direct collection and analysis of  $\text{CO}_2$  outgassed from the water surface allows this flux to be largely disconnected from the other components of dissolved inorganic carbon in streamwater. This is one of the main problems associated with indirect methods, in which the isotopic composition of  $\text{CO}_2$  gas in equilibrium with DIC can be calculated assuming that a steady state or quasi-steady state exists between evaded  $\text{CO}_2$  and  $\text{CO}_2$  produced by within-stream production (Mayorga et al. 2005). Although a dynamic equilibrium exists between  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and free  $\text{CO}_2$  in streamwater of low pH and high DOC (such as that characteristic of peatland drainage systems), most of the DIC is present in the form of free  $\text{CO}_2$  (Wetzel 1983). A method that avoids chemical manipulation of the carbonate system and does not make assumptions about equilibrium kinetics is therefore preferable and more likely to provide isotopic data that directly links  $\text{CO}_2$  lost by evasion to its sources. The method may also be applied to a range of biogeochemically different aquatic environments, including high pH systems where carbonate dissolution is an important component of the equilibrium dynamics of DIC.

The data presented in Table 1 lists the first direct measured values of  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  of  $\text{CO}_2$  lost by evasion from water surfaces. The data demonstrate the reproducibility of the method; despite the replicates from Site 5 just failing to overlap at  $2 \sigma$ , the other set of replicates had identical  $^{13}\text{C}$  and  $^{14}\text{C}$  contents at the  $<1\text{-}\sigma$  level. A possible reason for the small difference in the carbon isotope contents of the replicates from Site 5 could be due to inadequate scrubbing of the chamber prior to allowing the  $\text{CO}_2$  to build up. This would result in a small component of atmospheric  $\text{CO}_2$  contributing to the first samples in each pair of replicates from the 2 sites (i.e. M1 and M3). Given a pump rate of  $600 \text{ mL min}^{-1}$  and assuming complete removal of the  $\text{CO}_2$  from the gas stream, we calculated that scrubbing the equivalent of 2 chamber volumes would leave an estimated  $\sim 0.40$  mL of atmospheric  $\text{CO}_2$  in the chamber (assuming the chamber had an initial atmospheric  $\text{CO}_2$  concentration of 380 ppm). Using mass balance and assuming an atmospheric  $^{14}\text{C}$  concentration of  $\sim 107\%$  Modern (Levin and Kromer 2004) and  $^{13}\text{C}$  of  $-9\text{‰}$ , we can correct the first replicate of each of the 2 sets of samples for this possible source of contamination. For sample M1, the correction resulted in a

slightly older  $^{14}\text{C}$  age ( $1550 \pm 29$  BP) and a shift in the  $^{13}\text{C}$  value to  $-21.5\text{‰}$ ; however, the results remain identical (at  $<2\sigma$ ) to those of the replicate M2. When the results for M3 are corrected for this small amount of contamination, the new results ( $^{14}\text{C}$  age of  $930 \pm 26$  BP and  $^{13}\text{C}$  of  $-21.6\text{‰}$ ) become identical to the replicate (M4) at the  $<1\text{-}\sigma$  level. Consequently, we consider that a greater amount of chamber air should be scrubbed prior to the  $\text{CO}_2$  build-up stage, and recommend a minimum of the equivalent of 5 volumes be scrubbed. Although this would lead to a longer scrubbing period in the field, this can be reduced by using a pump with a flow rate greater than  $600 \text{ mL min}^{-1}$ .

Interestingly, the  $^{14}\text{C}$  results suggest that the  $\text{CO}_2$  is relatively old. This implies that the  $\text{CO}_2$  is either derived from deep (old) peat or that it contains the signature of carbonates that are known to occur in thin bands beneath the peat bog. Peat has been accumulating at Auchencorth Moss since the end of the last ice age ( $\sim 10,000$  BP) and reaches up to 10 m in thickness. The possibility that the  $\text{CO}_2$  is derived from the peat is also supported by the  $\delta^{13}\text{C}$  values, which are all very similar and consistent with an allochthonous, soil-derived source for  $\text{CO}_2$ . The values also fall in the middle of the range of values ( $-17.2$  to  $-25.2\text{‰}$ ) reported for soil atmosphere  $\text{CO}_2$  samples collected from deep peat and riparian soil in the Brockly Burn catchment, NE Scotland (Palmer et al. 2001). Clearly, more data are required to investigate this further; the main aim here is to present the method rather than to hypothesize further about the origins of  $\text{CO}_2$  lost by evasion from peatland surface waters.

In conclusion, the ability to  $^{14}\text{C}$  date  $\text{CO}_2$  lost by evasion from surface waters and in other atmospheric samples using zeolite molecular sieves linked to a suitable collection system has the potential to improve our understanding of the C cycle; specifically, the technique is able to identify different sources of  $^{14}\text{C}$ -enriched or depleted atmospheric  $\text{CO}_2$ . The direct method also removes some of the uncertainty associated with the indirect “gas stripping” method. Isotopic analysis of  $\text{CO}_2$  clearly has the potential to provide answers to key questions about the cycling of C in the terrestrial environment.

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