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Isotope \(^{(14}\text{C} \text{and} \ 13\text{C})\) analysis of deep peat CO\(_2\) using a passive sampling technique

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Abstract

We developed and tested a new method to collect CO\(_2\) from the surface to deep layers of a peatland for radiocarbon analysis. The method comprises two components: i) a probe equipped with a hydrophobic filter that allows entry of peat gases by diffusion, whilst simultaneously excluding water, and, ii) a cartridge containing zeolite molecular sieve that traps CO\(_2\) passively.

We field tested the method by sampling at depths of between 0.25 and 4 m at duplicate sites within a temperate raised peat bog. CO\(_2\) was trapped at a depth-dependent rate of between \(~0.2-0.8\) ml d\(^{-1}\), enabling sufficient CO\(_2\) for routine \(^{14}\text{C}\) analysis to be collected when left in place for several weeks. The age of peatland CO\(_2\) increased with depth from modern to \(~170\) BP for samples collected from 0.25 m, to \(~4000\) BP at 4 m. The CO\(_2\) was younger, but followed a similar trend to the age profile of bulk peat previously reported for the site (Langdon and Barber, 2005). \(\delta^{13}\text{C}\) values of recovered CO\(_2\) increased with depth. CO\(_2\) collected from the deepest sampling probes was considerably \(^{13}\text{C}\)-enriched (up to \(~+9\) \%) and agreed well with results reported for other peatlands where this phenomenon has been attributed to fermentation processes. CO\(_2\) collected from plant-free static chambers at the surface of the mire was slightly


1. Introduction

Peatlands contain vast stores of carbon and have the potential to significantly enhance the current rate of increase in atmospheric CO$_2$ if destabilization were to occur. As a result, the carbon balance of peatlands has been the focus of much research in recent years. Radiocarbon analysis of peatland organic materials (e.g. macrofossils) has been widely applied to determine peat growth and carbon accumulation rates (e.g. Tolonen and Turunen, 1996; Oldfield et al., 1997).

Few studies have dated CO$_2$ within deep peat, perhaps due to technical challenges during sampling, and we know of no study where both the profile of peat CO$_2$ and the surface efflux from the same peatland have been dated. However, information on the age of surface and deep peat gases such as CO$_2$ can provide valuable insights into their source and contribution to total peatland CO$_2$ flux; ultimately these data will provide a more complete understanding of the peatland carbon balance.

Several studies have previously reported the radiocarbon ($^{14}$C) content of CO$_2$ dissolved in the permanently water-logged layers of peatlands, but generally results have been few and
unreplicated (Clymo and Bryant, 2008). In these studies, dissolved CO$_2$ has consistently been found to be younger than the surrounding peat. For example, in Canadian boreal peatlands Aravena et al. (1993) and Charman et al. (1994) found peat CO$_2$ to be between 500 and 2000 years younger than the adjacent peat. Another study performed in an oceanic peatland in southwest England (Charman et al., 1999) reported that peat CO$_2$ was younger than the surrounding peat by between ~ 800 and 1500 years. Suggested mechanisms for this difference include the downward migration of younger carbon by mass flow or diffusion, and as dissolved organic carbon or CO$_2$ (Aravena et al., 1993; Charman et al., 1999; Clymo and Bryant, 2008). However, the methods employed to recover deep peat CO$_2$ in several of these studies required drawing gas into evacuated flasks which could have contributed to the downward transport of younger CO$_2$ (Aravena et al., 1993). Charman et al. (1999) also discuss the possibility of atmospheric CO$_2$ contaminating samples with the method that they employed. The gas sampling approach utilised by Clymo and Bryant (2008) avoided similar issues since it was not reliant on a vacuum to recover samples, however, Clymo’s method required the manufacture of specialised sampling equipment and a somewhat lengthy installation and sampling procedure. Therefore, our primary aim was to develop a new method to collect CO$_2$ from the deep layers of a peatland for carbon isotope analysis which minimizes site disturbance during installation and is simple and inexpensive to construct, thus reducing some of the barriers to greater replication.

Like deep peat CO$_2$, few studies have analysed the $^{14}$C content of CO$_2$ emitted from the surface of a peatland, yet the $^{14}$C content of the surface efflux could provide valuable information on the age of the CO$_2$ emitted and the contribution of deep peat CO$_2$ to the surface efflux. The lack of studies may be due to technical difficulties in collecting samples because the concentration of CO$_2$ at the mire/atmosphere boundary is likely to be considerably less than that found within the peat itself, due to dilution with air. However, Bol and Harkness (1995), Gaudinski et al. (2000) and Hardie et al. (2005) all report molecular sieve based sampling methods which should be
suitable for the collection of CO$_2$ emitted from the surface of a peatland, although to our knowledge, no published results are available for the $^{14}$C content of CO$_2$ emitted from the surface of peatlands.

Recently, a new method to recover CO$_2$ for $^{14}$C analysis by passive trapping with zeolite molecular sieve to date soil respired CO$_2$ was reported (Garnett et al., 2009). Here, we describe and test a development of this method that utilises a simple sampling probe which can be inserted into any peat profile to a range of depths. At the peat surface the probes are attached to a molecular sieve cartridge to enable passive sampling of deep peat CO$_2$. In addition, we used a chamber-based passive sampling method (Garnett et al., 2009) to characterise the isotopic composition of CO$_2$ emanating from the peatland surface. Our aims were i) to test the ability of the new method to collect CO$_2$ from a range of depths in a deep peat profile for $^{14}$C analysis, and, ii) to use measurements of the radiocarbon age and $\delta^{13}$C of deep peat CO$_2$ and surface CO$_2$ efflux to provide information on the contribution of deep peat to the overall surface CO$_2$ emissions.

2. Methods

2.1 Molecular sieve cartridge and sampling probe design

The new method to collect deep peat CO$_2$ for radiocarbon analysis is composed of two parts; a sampling probe and a molecular sieve cartridge (MSC). The sampling probes (Fig. 1) were constructed from stainless steel tubing (6 mm OD) that were cut to lengths a few cm longer than the depths of peat that were required to be sampled. To permit convenient transport of the longest probe (4 m) to the field site the tubing was spilt into two sections that were easily connected or disconnected by way of a stainless steel union (Swagelok, USA). The top 5 cm of each probe was bent to an angle of 90 degrees allowing it to run parallel with the peatland
surface. This facilitated easy sampling by connection of a MSC via an auto-shutoff Quick Coupling (Colder Products Company, USA). At the opposite end of the sampling probe (that which would be placed into the peat) the steel tubing was sealed using a bolt (Fig. 1). Approximately 10 cm above the base of the sampling probe, six holes (2 mm diameter) were made through which peat gases could enter and make their way to the surface on the inside of the steel tubing. The holes were covered by a length (5 cm) of gas permeable hydrophobic tubing (Accurel PP V8/2 HF, Membrana GmbH, Germany; Gut et al., 1998) thus allowing peat gases but not water, to enter the sampling probe. All joins were covered with heat shrink and a rubber sealant (Plasti-dip, Minnesota, USA) to ensure that water could not gain entry, and leak-tested prior to installation at the field site.

We used the same design of MSC that was previously used in pump-based (Hardie et al., 2005) and passive (Garnett et al., 2009) CO₂ sampling methods, both developed for trapping soil-respired CO₂ for ¹⁴C analysis. The design of the MSC has been described in detail by Hardie et al. (2005), but briefly, consisted of a quartz glass cartridge containing ~ 3-4 g of Type 13X zeolite molecular sieve (1/16” pellets, BDH, UK) held within a central chamber using quartz wool. At both ends of the cartridge, auto-shutoff Quick Couplings were attached via short lengths of PVC tubing (Tygon, Fisher, UK). Although the couplings seal automatically when not connected we also used plastic clips (WeLoc®, Scandinavia Direct, UK) placed across the PVC tubing to form an additional seal when necessary. The MSCs were charged by heating (500 °C) whilst under high vacuum (10⁻³ mb) for ~ 1.5 hours prior to use after which they were allowed to cool and filled with high purity N₂ to just above ambient pressure.

2.2 Experimental design
Field testing aimed to determine whether the sampling probes provided sufficient CO$_2$ for $^{14}$C analysis and in addition, whether the CO$_2$ collected was representative of deep peat CO$_2$ at the depth being sampled. A simple measurement of the volume of recovered CO$_2$ would indicate whether sufficient sample had been collected for $^{14}$C analysis. However, to assess whether the recovered CO$_2$ was isotopically representative of the peat gas at the depth being sampled was less easy, as we had no independent knowledge of the isotopic composition of the peat CO$_2$ for this site. The criteria that we adopted to test the method firstly involved the collection of duplicate samples with the assumption that deep peat CO$_2$ should have a similar carbon isotopic composition when collected from adjacent locations. Secondly, we compared our results with what we would expect based on the small number of measurements that have previously been reported for deep peat CO$_2$. For example, previous studies have shown consistent increases in the age and $\delta^{13}$C of deep peat CO$_2$ with increasing depth (Clymo and Bryant, 2008), and reported that deep peat CO$_2$ was slightly younger compared to the age of the surrounding peat (e.g. Aravena et al., 1993; Charman et al., 1994, 1999; Clymo and Bryant, 2008). Finally, a third component of the testing involved a laboratory-based experiment: a standard CO$_2$/air mixture of known CO$_2$ concentration and isotopic composition, contained within a large air-tight barrel, was sampled using the probes to test that representative samples of CO$_2$ were recovered.

Field testing was performed at Langlands Moss, an ombrotrophic raised peat bog near Glasgow, UK (55°44’05.9” N, 4°10’26.1”W). Sampling probes were inserted to four depths (0.25, 1, 2 and 4 m) at two sampling sites (Sites A and B) located approximately 20 m apart. Installation of the probes was easily accomplished by simply pushing them vertically into the peat surface until the required depth was reached, with only the sampling end of the probe being exposed (Fig. 1). For at least 2 d prior to installation of the probes, atmospheric CO$_2$ was passively scrubbed from inside the stainless steel tubes by covering the hydrophobic filter with a rubber seal and attaching a cartridge filled with soda lime to the coupling. Only immediately prior to insertion of each
probe into the peat was the soda lime cartridge and rubber seal removed, thus minimizing contamination from atmospheric CO$_2$. Following installation, sampling probes were left for 1 month before sampling commenced.

In addition to samples collected from the probes, we captured CO$_2$ emitted from the bog surface using a chamber-based passive sampling method (Garnett et al., 2009). This method used the same MSCs utilised for the sampling probes, which were attached to each closed chamber with identical couplings. The chambers consisted of circular plastic soil pipe (10 cm ID x 15 cm length) that was left open at one end (for contact with the peat surface) and sealed at the other. Three Quick Couplings were installed into the side of each chamber, one of which contained a hydrophobic filter (Accurel PP V8/2 HF, Membrana GmbH, Germany; Gut et al., 1998). Each of the chambers were pushed into the surface of the peat to a depth of 5 cm at the same two sites being used to test the deep peat sampling probes (all vegetation including moss was removed one month before sampling commenced). Before collection of surface CO$_2$, each chamber headspace was scrubbed to remove atmospheric CO$_2$ using a soda lime based scrubbing system (Hardie et al., 2005). The chambers were then left in place for one month prior to sampling.

Sampling probes were left in place to trap deep peat CO$_2$ continuously for a total of ~ 2.5 months (Site A: 3 October, 2008 to 9 December, 2008; Site B: 3 October, 2008 to 16 December, 2008). Chambers were sampled continuously with MSCs for 1 week only and were then removed. A total of three sets of chamber samples were collected at the start (3-10 October, 2008), middle (26 November-3 December, 2008) and end (9-16 December, 2008) of the experiment. On at least two occasions per month, including when chamber MSCs were exchanged, site variables including water table depth, air and soil temperatures were recorded. In addition, over the course of the experiment we made multiple measurements of CO$_2$ concentration inside the closed chambers, and measured surface CO$_2$ emissions from the mire, using an identical closed chamber.
that was only placed on the mire surface during flux measurement (~ 10 minutes). An EGM-4
infrared gas analyzer (PP Systems, UK) was used for all field CO₂ measurements. Immediately
after the final chamber MSC had been disconnected at the end of the experiment a further sample
of chamber CO₂ was collected from both sites using a pump-based molecular sieve sampling
system (Hardie et al., 2005).

In the laboratory experiment, sampling probes identical to those used in the field, were inserted
via a large rubber bung into a 30 L air-tight plastic barrel which contained air with an elevated
CO₂ concentration. The concentration (~ 24000 ppm) and δ¹³C (-24.6 ‰) of the CO₂ in the
air/CO₂ mix had previously been determined (the former using an IRGA, and the latter from sub-
samples collected from the barrel using an evacuated flask). For the laboratory test, MSCs were
used to passively trap CO₂ from the barrel using sampling probes of different lengths. This
experiment addressed two issues: first to test whether the sampling probe method collected
representative samples of CO₂ by comparison of the MSC-collected samples with the evacuated
flask samples. Second, to verify that the rate of CO₂ trapping obeyed Fick’s law; this would
permit estimation of the CO₂ concentration in the atmosphere being sampled from the CO₂ trap
rate. Following Bertoni et al. (2004), we used an expression derived from Fick’s law which
cconcerns the kinetics of molecular movement along a gradient (towards an absorbent) when the
movement is restricted to the inside of a tube:

\[ C_i = \frac{Q_i \times L}{S \times t \times D_i} \]

Equation 1

where \( C_i \) represents the CO₂ concentration of the environment being sampled, \( Q_i \) is the amount
of CO₂ trapped during time \( t \), \( L \) and \( S \) are the length and cross-sectional area of the entire
sampling probe (from gas inlet to molecular sieve), and \( D_i \) is the diffusion coefficient of CO₂ in
air (Bertoni et al., 2004).
2.3 CO₂ recovery and isotope analysis

After each sampling occasion (field or laboratory), clips were placed on either end of each MSC before being disconnected and returned to the NERC Radiocarbon Facility for CO₂ recovery.

Sample CO₂ was desorbed by heating (500 °C) the molecular sieve while attached to a vacuum rig (see Hardie et al., 2005). The gas evolved was dried by passing through a slush trap (mixture of dry ice and industrial methylated spirits; -78°C) and then purified by trapping in liquid N₂.

The quantity of CO₂ recovered was measured in a calibrated volume before being split into sub-samples for analysis.

One sub-sample was analysed for δ¹³C (¹³C/¹²C ratio in ‰ units relative to the standard Vienna Pee Dee Belemnite; VPDB) using a dual inlet isotope ratio mass spectrometer (VG Optima, Micromass, UK) at the NERC Radiocarbon Facility. A second sub-sample was reduced to graphite using Zn/Fe reduction (Slota et al., 1987) and analysed by accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK (Freeman et al., 2007). ¹⁴C results were normalised to a δ¹³C of -25 ‰ to account for mass-dependant fractionation, and expressed as conventional radiocarbon ages (years BP) and %modern (Stuiver and Polach, 1977). Following convention, measurement uncertainties associated with isotope concentrations are expressed as standard deviations.

3. Results

A summary of site characteristics including temperature, water table depth and CO₂ flux rates recorded during the sampling period is provided in Table 1. Both sampling locations were
similar in terms of air and soil temperature, mean water table depth and CO$_2$ flux rate, however, CO$_2$ concentration in the closed chamber was consistently higher at Site B.

After ~ 2.5 months exposure, MSCs attached to sampling probes had trapped between 15 and 55 ml of CO$_2$, easily sufficient for $^{14}$C analysis. Trapping rates ranged from a minimum of ~ 0.2 ml d$^{-1}$ at 0.25 m depth to a maximum of 0.8 ml d$^{-1}$ at 2 m depth (Fig. 2a). Since under the known conditions of the laboratory experiment we found a very strong agreement between measured and theoretical CO$_2$ trapping rate (based on Fick’s law; Fig. 3), we used equation 1 to convert the CO$_2$ trap rates measured using the sampling probes into estimates of CO$_2$ concentration within the deep peat (assuming the diffusion coefficient of CO$_2$ in the probe gas to be the same as in air). Results showed that CO$_2$ concentration in the peat gas increased linearly from ~ 1 % at 25 cm depth, to between 14 and 19 % at 4 m (Fig. 2b).

Carbon isotope ($\delta^{13}$C and $^{14}$C) results for both deep peat CO$_2$ and chamber CO$_2$ samples (collected both passively and dynamically using the pump-based method) are presented in Table 2. Consistent with previous observations (Garnett et al., 2009), we found a ~ 4 ‰ offset for $\delta^{13}$C measurements between the pumped and final set of samples collected passively with a MSC (CHAMBER A-3 and CHAMBER B-3) which we attribute to fractionation during passive trapping (Table 2). This difference in $\delta^{13}$C was also observed between evacuated flask and passive MSC samples collected during the laboratory test of the sampling probes (mean = 4.0 ± 0.2 ‰ SD; n = 4). The $\delta^{13}$C results for deep peat CO$_2$ and chamber CO$_2$ illustrated in Figure 4a have therefore been adjusted to account for this offset. The results show that chamber CO$_2$ had a $\delta^{13}$C of ~ -22 to -25 ‰, whilst within the peat profile, the $\delta^{13}$C of CO$_2$ increased from ~ -13 ‰ (Site A) and -10 ‰ (Site B) at 0.25 m, to ~ +9 ‰ in the 4 m samples at both sites (Fig. 4a). $^{14}$C age of deep peat CO$_2$ increased with depth from modern (Site A) and 169 ± 37 BP (Site B) at
0.25 m, to ~4000 BP at 4 m depth. All chamber $^{14}$C concentrations fell within the range 106.51 to 108.08 % modern (Table 2; Fig. 4b).

4. Discussion

4.1 Sampling probe technique

Our main aim was to test a new method to collect deep peat CO$_2$ for carbon isotope measurement, with tests first focusing on whether sufficient CO$_2$ could be recovered for analysis, and whether this was representative of CO$_2$ produced at the peat depths being sampled. Previous tests on the use of Type 13X molecular sieve have verified its reliability for collecting samples of CO$_2$ for both $^{13}$C and $^{14}$C analysis (Bauer et al., 1992). In addition, the MSCs that we utilised have been shown not to suffer from contamination, sample carry-over (hysteresis), or isotopic fractionation when used with a pump-based sampling system (Hardie et al., 2005). Subsequent tests by Garnett et al. (2009) showed that the same MSC could be used reliably to passively trap soil-respired CO$_2$ for $^{14}$C analysis. Consequently, we consider it reasonable to assume that the MSC cartridge performed equally well when attached to the steel sampling probes, and therefore our tests were essentially investigating the application of the probes.

According to Fick’s law (equation 1), the rate of CO$_2$ trapping in an absorbent is dependent on a number of factors including exposure time, the CO$_2$ concentration of the environment being sampled and the distance between the source and absorbent (Bertoni et al., 2004). Our field test results showed that after ~2.5 months the MSCs had trapped between 15 and 55 ml CO$_2$, suggesting that even at the lowest trap rates, sufficient CO$_2$ (~ 5 ml) for both $^{13}$C and $^{14}$C analysis could have been recovered after just one month of sampling. Alternatively, since Garnett et al. (2009) have shown that the MSCs can passively trap at least 120 ml CO$_2$, the MSCs could well
have continued sampling for at least ~ 6 months (i.e. before saturation occurs). Clearly the
method is easily capable of providing sufficient CO$_2$ for carbon isotope analysis, and the CO$_2$
capacity of the MSCs allows for uncertainty in estimating the required exposure time in
applications where prior knowledge of the CO$_2$ concentration of the environment being sampled
is not available. That we found very good agreement between measured (laboratory experiment)
and theoretical (estimated from Fick’s law) rates of CO$_2$ trapping is particularly valuable for
estimating the required sampling time (e.g. for different lengths of sampling probes). However,
our values for %CO$_2$ in the peat gas (Fig. 2b) could be underestimates if the rate of CO$_2$ removal
by the molecular sieves was greater than the rate that CO$_2$ was replenished around the sampling
probe (i.e. from CO$_2$ production and diffusion within the peat). Indeed, Clymo and Bryant
(2008) reported higher CO$_2$ concentrations in similar depths at another Scottish ombrotrophic
mire, and underestimates of the CO$_2$ concentration by probe samples may explain the anomalous
observation that the static chambers on the surface of the mire were more concentrated in CO$_2$
than the peat at 0.25 m depth (Table 1 and Fig. 2b).

Atmospheric CO$_2$ was a possible source of contamination in the probes prior to their insertion
into the peat and therefore we attempted to remove it by scrubbing with soda lime. However, we
calculate from the volume of the sampling probes and ambient CO$_2$ concentration, that the
maximum volume of atmospheric CO$_2$ that could have caused contamination at the beginning of
the experiment, would only have been ~ 0.02 ml. This represented less than 0.2 % of the CO$_2$
recovered from any of the MSCs over the course of the experimental period. Thus, even if we
had not removed this contaminant at the start of the experiment our results would have been
affected by an amount considerably less than the precision of the $^{14}$C measurements.

In their study of a raised bog Clymo and Bryant (2008) found very close agreement between
replicates of peat CO$_2$ from the same depth, and therefore we considered that a test of the
reliability of the sampling probes was through comparison of results for duplicate samples. We similarly found very good agreement between our duplicate samples from different depths. Closest agreement occurred in the deeper samples, with for example, $^{14}$C concentrations for duplicate samples from the 2 m and 4 m depths agreeing to within 1 $\sigma$. That there was a greater difference in the results for samples closer to the mire surface may be due to variations in contributions of recent carbon inputs that have occurred during a period when atmospheric $^{14}$C has been relatively variable (i.e. due to bomb-$^{14}$C), or alternatively, it may be a result of exchange between the shallower peat layers and the atmosphere. Waldron et al. (1999) measured the $^{13}$C isotope of deep peat CO$_2$ and similarly found that variation between sites decreased with increasing depth.

Our results collected using the passive sampling approach are similar to previous studies. Firstly, as also reported by Clymo and Bryant (2008), we found that the $^{14}$C content of deep peat CO$_2$ showed a consistent decrease with depth. We also found that the age of deep peat CO$_2$ followed a similar trend, but was consistently younger, compared to bulk peat that had been sampled from the same raised mire (Fig. 4b); an observation that has also been reported for other peatlands by Clymo and Bryant (2008), Aravena et al. (1993) and Charman et al. (1994, 1999). Although there was a difference between the $^{14}$C contents at the same depths between our results and those of Clymo and Bryant (2008), this may well be due to site differences such as peat accumulation rates, for example, total peat depth at our study site was in excess of 8 m, while the peatland of Clymo and Bryant (2008) only extended to a depth of ~ 7 m. For $\delta^{13}$C, there was even closer agreement between the relationship with depth for our results and previous studies. For example, at 4 m depth, we found that deep peat CO$_2$ had a $\delta^{13}$C of between +8.6 to +9.2 $\%$, while for the same depth at their peatland Clymo and Bryant (2008) report values of between +8.7 and +9 $\%$. Although both sets of results are from different sites, it is reasonable to suppose that the same processes responsible for producing the trend of increasing $\delta^{13}$C with depth are occurring, and
therefore we might expect similar δ\(^{13}\)C profiles if both sampling approaches collected deep peat CO\(_2\) that was representative of the depths sampled.

The third test of the sampling method was performed by way of a laboratory experiment using a standard air/CO\(_2\) mixture. Although we did not measure the \(^{14}\)C content, we found that the δ\(^{13}\)C of all passively collected MSC samples was identical (when considering the analytical precision of the measurement) at all probe lengths tested. Furthermore, there was very good agreement between the measured trapping rate and the theoretical rate based on Fick’s law, when taking into account the dimensions (inner diameter and length) of the sampling probes. Comparison of the δ\(^{13}\)C values of evacuated flask and passive MSC samples confirmed previous observations that a ~ 4 ‰ fractionation occurs during passive trapping; isotopic fractionation has been reported for molecular sieves (Garnett et al., 2009) and when trapping CO\(_2\) in a hydroxide absorbent (Davidson, 1995), and is likely a result of fractionation during diffusion through air.

The adjustment of the δ\(^{13}\)C results for this fractionation effect may slightly increase the uncertainty in δ\(^{13}\)C values, but the results of the laboratory test suggest that the adjustment factor does not vary with probe length. Furthermore, the corrected δ\(^{13}\)C results from the field samples agree remarkably well with values reported by others e.g. Clymo and Bryant (2008). It should also be remembered that following convention, \(^{14}\)C results were corrected for mass-dependent fractionation by normalising to a δ\(^{13}\)C of –25 ‰, which will have accounted for fractionation of the \(^{14}\)C isotope during passive sampling.

4.2 Implications for peatland carbon emissions

As reported above, we found trends in the \(^{14}\)C and δ\(^{13}\)C of peat CO\(_2\) that were very similar to results from the few other peatlands where the isotopic composition of deep peat CO\(_2\) has been studied. That peat CO\(_2\) was also consistently younger at our site compared to the bulk peat
supports previous suggestions that it is derived not only from the surrounding peat, but that it also contains a component that has migrated from higher in the peat profile. It seems likely (as reported by others), that fermentation processes such as acetoclastic methanogenesis (Aravena et al., 1993; Charman et al., 1999) or hydrogenotrophic methanogenesis (Whiticar et al., 1986) are taking place at depth, since these processes would result in the highly $^{13}$C-enriched CO$_2$ observed at depth within the peatland at Langlands Moss.

That we found chamber CO$_2$ to be slightly $^{14}$C-enriched relative to the contemporary atmosphere may suggest that the surface efflux was predominantly derived from carbon fixed within the last few years, and that CO$_2$ derived at depth contributed little to the surface efflux. This explanation seems to fit with current peatland carbon balance models. However, some CO$_2$ derived from deep in the peat profile may well escape from the surface, and slight differences in the rate of CO$_2$ exchange between the upper layers of the peatland and the atmosphere may be one explanation for the divergence in results between our two sampling sites. Similarly, since Wahlen et al. (1989) reported that $^{14}$C results of methane emanating from the peatland surface showed that aged carbon in methane contributed to surface gas emissions, it can probably be expected that surface emissions will also contain a component of old CO$_2$. Indeed, if CO$_2$ derived from deep peat contributed only a few percent to the surface emission, it is unlikely that we would be able to detect this simply from a few $^{14}$C measurements of surface CO$_2$ emissions unless the contribution of pre-bomb carbon was so great that it caused the $^{14}$C content of surface emissions to fall below the $^{14}$C content of the contemporary atmosphere, as recently demonstrated within an arctic ecosystem (Schuur et al., 2009).

The surface chamber $\delta^{13}$C results show that CO$_2$ became increasingly $^{13}$C-enriched over the course of the experiment, while a less significant but consistent difference is suggested by chamber $^{14}$C results. At both Sites A and B, chamber CO$_2$ at the end of the experiment was
slightly depleted in $^{14}$C relative to the beginning, while $\delta^{13}$C increased significantly by between 1.6 to 3.1 $\%$ between October and December. This observation is consistent with an increased contribution to the chamber of CO$_2$ that was both depleted in $^{14}$C and enriched in $^{13}$C. Since the sampling period began in autumn and ended in early winter, and because the sampling plots were plant-free, one explanation may be that the relative proportion of a $^{14}$C-depleted and $^{13}$C-enriched component to chamber CO$_2$ increased as a result of a smaller contribution from the decay of organic matter at the surface of the peatland (due to lower temperatures). Two potential sources of relatively $^{14}$C-depleted and $^{13}$C-enriched CO$_2$ that could plausibly explain the observed change in isotopic composition of chamber headspace (and would presumably not be greatly affected by seasonal changes), are either atmospheric CO$_2$ or deep peat CO$_2$. In terms of the former, there is likely to have been at least some atmospheric CO$_2$ in the chamber because its base (inserted to 5 cm depth below the peat surface) did not always extend below the water table (Table 1). Alternatively, the surface efflux could contain a greater relative contribution from deep peat CO$_2$ during colder months because, unlike CO$_2$ production in the surface layers, deep peat CO$_2$ is likely to be less affected by seasonal changes (for example, Clymo and Pearce, 1995, state that gas concentration profiles in the catotelm change little with season, presumably due to a much smaller variation in annual temperature at depth).

Isotope mass balance calculations suggest that the observed isotopic changes in chamber CO$_2$ cannot be explained by a greater component of atmospheric CO$_2$ in the chambers because this would require an increased atmospheric contribution of at least 8-15 $\%$ (based on $\delta^{13}$C calculations; even greater contributions are required to satisfy the $^{14}$C results). However, the maximum contribution of air CO$_2$ in the chamber cannot have been more than about 1.6 $\%$ (assuming an ambient atmospheric CO$_2$ concentration of 380 ppm and a total chamber CO$_2$ concentration of ~ 24700 ppm; Table 1). Moreover, the observed isotopic shifts in chamber CO$_2$ concentration can be explained by contributions of deep peat-derived CO$_2$, requiring for
example, a fractional increase in chamber CO₂ (in December relative to October) of 2-8% being derived from deep peat CO₂ with an average isotopic composition of that measured at 2 m. Interestingly, Hirsch et al. (2002) similarly found evidence of a shift to a greater release of older (pre-bomb) carbon in soil respiration when moving from summer to autumn during a study of deep soil respiration in a boreal forest. They at least partly attributed this shift to a relative increase in the contribution of deep soil CO₂ due to the surface litter layer becoming colder than the deep soil (and thus a decrease in CO₂ produced from younger, more shallow soil).

We have shown from respiration chamber results that it is likely that the proportion of total CO₂ efflux derived from deep peat CO₂ increased between October and December, however, we cannot estimate a total flux from deep peat CO₂ using these results. But, using our measurements of average CO₂ efflux at the study site (Table 1) we can suggest that the emission of deep peat CO₂ was at least ~ 0.2 to 1.2 mg C m⁻² hr⁻¹. Although further investigation is required to support these findings, it seems likely that deep peat CO₂ does contribute significantly to the surface efflux from this peatland, and that the contribution it makes to the total flux varies seasonally.

5. Conclusions

1. The technique of passive sampling using probes coupled to zeolite molecular sieve cartridges is inexpensive, easy to install and operate, and provides a reliable method to recover deep peat CO₂ for radiocarbon analysis and δ¹³C measurement.

2. Probes of a wide range of lengths can be used, although it should be noted that the rate of trapping will decline with increasing probe length thereby increasing the exposure time required to provide sufficient CO₂ for analysis; this can be easily estimated using Fick’s law.
3. Profiles of decreasing $^{14}$C content and increasing $\delta^{13}$C of peat CO$_2$ with depth compared well with results reported for other peatlands. Peat CO$_2$ was younger than bulk peat at the same depth, suggesting that although being predominantly derived from the surrounding peat, there was a contribution to the CO$_2$ pool by carbon produced from younger sources closer to the peatland surface.

4. The carbon isotope composition of surface chamber CO$_2$ samples suggested that the majority of the surface efflux was derived from recently fixed carbon. However, differences in the isotopic composition between the start and end of the sampling period are most likely explained by differing contributions from deep peat-derived CO$_2$ to surface emissions.

5. The sampling probes were designed for recovering dissolved CO$_2$ from deep peats. However, since peat is composed typically of 90% water, the probes could also be used to collect CO$_2$ for carbon isotope analysis from other environments including aquatic systems (lakes/rivers).

Acknowledgments

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References


Berto


Langdon, P.G., Barber, K.E., 2005. The climate of Scotland over the last 5000 years inferred from multiproxy peatland records: inter-site correlations and regional variability. Journal of Quaternary Science 20, 549-566.


Table 1 Temperature (air and soil at 10 cm), water table depth (relative to peat surface), surface

CO₂ efflux and static chamber CO₂ concentration from plant-free plots. Measurements were
performed between ~10 am and 11:30 am at both sampling sites during field visits throughout
the course of the experiment (October to December 2008).

<table>
<thead>
<tr>
<th></th>
<th>Site A</th>
<th>Site B</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Minimum</td>
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<tr>
<td>Air temperature (°C)</td>
<td>7.8</td>
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<tr>
<td>Soil temperature at 10 cm (°C)</td>
<td>6.3</td>
<td>1.3</td>
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<tr>
<td>Water table depth (cm)</td>
<td>5.2</td>
<td>1.0</td>
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<tr>
<td>CO₂ efflux (mg CO₂-C m⁻² hr⁻¹)</td>
<td>14.7</td>
<td>7.1</td>
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<tr>
<td>Chamber CO₂ concentration (%)</td>
<td>3.46</td>
<td>2.47</td>
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</table>
Table 2 Carbon isotope results and radiocarbon publication codes for CO₂ collected from the deep peat sampling probes and surface chambers at Langlands Moss, East Kilbride, UK.

Radiocarbon results expressed as both %modern and conventional radiocarbon ages (CRA).

Sample identifiers differentiate CO₂ from i. different depths in the peat profile (PEAT CO₂), ii. soil surface chambers (collected by passive trapping with molecular sieve; CHAMBER) and, iii. soil surface chamber CO₂ (collected by dynamic trapping with molecular sieve; PUMPED). *NB δ¹³C values represent the actual CO₂ samples recovered and have not been corrected for fractionation during passive trapping.

<table>
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<tr>
<th>Site</th>
<th>Sample identifier</th>
<th>δ¹³CVPDB †</th>
<th>Publication code (SUERC-)</th>
<th>%modern ‡</th>
<th>CRA (BP) ‡</th>
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<tr>
<td></td>
<td></td>
<td>± 0.1 ‰</td>
<td></td>
<td>± 1 σ</td>
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<td>A</td>
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<td>105.47 ± 0.46</td>
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Figure captions

1. Schematic diagram of a deep peat sampling probe (not to scale). See text for further details.

2. CO₂ trap rate (a) and calculated % CO₂ of peat gas (b) collected by passive sampling with zeolite molecular sieve from the peat profiles at Langlands Moss, East Kilbride, UK. Site A (diamonds) and Site B (squares).

3. CO₂ trap rate for passive sampling probes of different lengths exposed to a fixed atmosphere (~ 24000 ppmv). Comparison of calculated (Fick’s Law) and actual measured results.

4. δ¹³C (a) and ¹⁴C content (b) of CO₂ collected passively using both sampling probes and surface chambers, at Langlands Moss, East Kilbride, UK. Results of carbon isotope analyses for bulk peat (made during an earlier study at Langlands Moss) are provided for reference (derived from Langdon and Barber, 2003). Note that δ¹³C values have been corrected for fractionation during passive trapping by applying a +4 ‰ correction factor (see text).
Figure

A  Coupling (to attach MSC)
B  PVC tubing
C  Impermeable seal (shrink fit and rubber sealant)
D  Hydrophobic filter (50 mm length, 8.5 mm OD, ID 5.5 mm)
E  6mm OD stainless steel tubing
F  Stainless steel ferrule
G  Gas exchange holes (2 mm diameter)
H  Steel bolt to seal end of tubing