Title: Bomb-^{14}C analysis of ecosystem respiration reveals that peatland vegetation facilitates release of old carbon

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Abstract:

The largest terrestrial-to-atmosphere carbon flux is respired CO_2. However, the partitioning of soil and plant sources, understanding of contributory mechanisms, and their response to climate change are uncertain. A plant removal experiment was established within a peatland located in the UK uplands to quantify respiration derived from recently fixed plant carbon and that derived from decomposition of soil organic matter, using natural abundance ^{13}C and bomb-^{14}C as tracers. Soil and plant respiration sources were found respectively to contribute ~ 36 % and between 41-54 % of the total ecosystem CO_2 flux. Respired CO_2 produced in the clipped ('soil') plots had a mean age of ~ 15 years since fixation from the atmosphere, whereas the ^{14}C content of ecosystem CO_2 was statistically indistinguishable from the contemporary atmosphere. Results of carbon mass balance modelling showed that, in addition to respiration from bulk soil and plant respired CO_2, a third, much older source of CO_2 existed. This source, which we suggest is CO_2 derived from the catotelm constituted between ~ 10 and 23 % of total ecosystem respiration and had a mean radiocarbon age of between several hundred to ~ 2000 years before present (BP). These findings show that plant-mediated transport of CO_2 produced in the catotelm may form a considerable component of peatland ecosystem respiration. The implication of this discovery is that current assumptions in terrestrial carbon models need to be re-evaluated to consider the climate sensitivity of this third source of peatland CO_2.

Keywords:

carbon cycling

CO_2

$\delta^{13}C$

isotope mass balance

mixing model

partitioning

peatland

radiocarbon

respiration

1. Introduction

The Earth's soils contain vast amounts of carbon. It has been estimated that globally, the top 1 metre of soils store ~ 1.5 Tt of carbon (Jobbagy and Jackson, 2000), nearly threefold that resident in terrestrial vegetation and double that currently in the atmosphere. One soil type in particular, peat, is responsible for storage of nearly a third of all soil carbon. Crucially, peatlands exist mainly at high latitudes (Gorham, 1991) where climate change is expected to produce the most pronounced effects (IPCC, 2007). If climate change perturbs carbon cycling in peatlands then these valuable carbon stores could become substantial carbon sources, thus augmenting the terrestrial greenhouse gas feedback to climate change. Ecosystem scale changes in carbon stocks depend on the balance between carbon sequestration *via* photosynthesis and carbon emission *via* autotrophic (e.g. plant) and heterotrophic respiration. Furthermore, recent evidence has shown that soil respiration may overcome increases in net primary production in response to climate change at a global scale (Piao et al., 2008) making the relative contribution of soil and plant respiration to ecosystem CO_2 fluxes an important determinant of carbon-climate feedbacks.

Many techniques have been used to partition component respiratory sources within an ecosystem including: root exclusion - the measurement of respiration in soil with roots being present and then again without (Lalonde and Prescott, 2007); component integration - the separation of litter, roots and sieved soil, followed by measurement of CO_2 production created by each component on an individual basis (Sapronov and Kuzyakov, 2007); girdling - a method that requires stripping a ring of bark from trees to xylem depth in order to prevent photosynthates reaching tree roots (Högberg et al., 2001); trenching - involving severing of roots from around a treatment plot to prevent input from trees and sub-canopy vegetation to below ground (Bond-Lamberty et al., 2004); clipping - a less invasive method than both the root exclusion and component integration techniques, that involves clipping above ground plant parts close to the ecosystem surface thus halting the supply of photosynthates to plant roots (Fu and Cheng, 2004; Grogan et al., 2001; Macdonald et al., 2004; Silvola et al., 1996a; Ward et al., 2009); and finally isotopic methods - the use of an enriched tracer or natural abundance of both stable and unstable (radioactive) isotopes of carbon (Gaudinski et al., 2000; Ostle et al., 2000).

None of these techniques is without caveat and therefore no perfect partitioning technique exists and most studies do acknowledge this fact (Subke et al., 2006). However, the use of isotopes as tracers is becoming increasingly popular (Hahn et al., 2006; Schuur and Trumbore, 2006) as they are potentially much less disruptive than removal or trenching experiments. Isotopes of carbon can provide valuable information regarding terrestrial carbon cycling (Amundson et al., 1998; Ehleringer et al., 2000; Harrison et al., 2000). For example, the use of bomb-produced radiocarbon as a tracer enables the identification and quantification of soil organic matter (SOM) turnover on decadal timescales e.g. (Harkness et al., 1986). A drawback of this technique is that it can underestimate soil carbon turnover if measurements of ^{14}C are made of bulk SOM only (Trumbore, 2000).

Within the last decade or so a number of studies have investigated the radiocarbon signature of respired CO_2 produced within terrestrial ecosystems (Gaudinski et al., 2000; Koarashi et al., 2002; Wookey et al., 2002). This has been made possible thanks to developments in radiocarbon analysis, such as the use of accelerator mass spectrometry (AMS), that allows relatively small volumes of CO_2 to be analysed, in tandem with novel techniques for CO_2 capture such as adsorption onto zeolite molecular sieve (Bol and Harkness, 1995; Hardie et al., 2005). Isotope measurements of CO_2, when combined with concomitant concentration data, provide empirical information that give an insight into processes that influence the storage and release of carbon within terrestrial ecosystems (Yakir and Sternberg, 2000). Most isotopic studies of soil respiration to date have focused attention on either forests (Gaudinski et al., 2000; Hahn et al., 2006; Koarashi et al., 2002; Schuur and Trumbore, 2006) or grasslands (Ostle et al., 2000; 2003). There have been few published studies investigating the ^{14}C signature of CO_2 evolved from the surface of a peatland, an exception being Jungner et al. (1995) who suggested that CO_2 emitted from a peat bog was ~ 100 %Modern (however they did not measure it directly). Considering peatlands are such valuable stores of carbon, and with current concerns over global warming in mind, there is an urgent need to better quantify carbon cycling rates within these ecosystems. Therefore, the primary objective of this study was to focus on biological transformations of carbon within the peatland environment with specific emphasis on using carbon isotope tracers to i) characterise the isotopic signature (both $\delta^{13}C$ and ^{14}C) of respired CO_2 emanating from a peatland

ecosystem and ii) partition ecosystem respiration into that which is derived from recently fixed plant carbon and that which is derived from older soil carbon sources in the bulk peat. This was achieved by analysis of CO_2 (both flux and isotopic composition) produced by a plant removal (clipping) experiment, isotope analysis of contemporary peatland plants and atmospheric CO_2, both in combination with carbon isotope mass balance modelling.

2. Materials and methods

2.1. Site Description

Moor House National Nature Reserve (UK National Grid ref. NY70 30) was chosen as the study site, being an area of blanket bog moorland considered representative of British upland terrain (Heal et al., 1978). Current mean annual precipitation for the Reserve is 2016 mm and mean annual temperature is 5.3 °C (at a height of 550 m) with climate falling into the subarctic oceanic classification (Evans et al., 1999). The blanket bog at Moor House is mostly ombrotrophic and the length of the growing season is approximately 180 days (Heal et al., 1978). Studies previously performed at Moor House have been many and diverse, and include investigations into: vegetation distribution (Eddy et al., 1969) and productivity (Forrest and Smith, 1975); dissolved organic matter (Billett et al., 2007; Tipping et al., 1999); microbiology (Briones et al., 1997); the natural variation in carbon isotope distributions within a range of soil types (Bol et al., 1999); and the effects of burning and grazing on carbon cycling (Garnett et al., 2000; Ward et al., 2007). All samples in this investigation were taken from an experimental site within the Reserve (Hard Hill; 54° 41' 28N, 2° 23' 57W – 587 m) characterised by gentle slopes, an average peat depth of ~ 1- 2 m, and a homogeneous cover of blanket bog/moorland vegetation (*Sphagnum* spp., *Calluna vulgaris* and *Eriophorum vaginatum*).

2.2. Experimental design

A Latin square design was established with treatments that involved manipulation of the three main plant functional groups (bryophytes, ericoid sub-shrubs, and graminoids) at the Hard Hill site in September 2003 (Ward et al., 2009). We were kindly allowed access to this experimental site in the growing season of 2005 specifically to use two of the treatments:

a. an ‘ecosystem’ treatment (control) that was composed of the original mire ecosystem (i.e. undisturbed soil and peatland plant species *Sphagnum* spp., *Calluna vulgaris* and *Eriophorum vaginatum*). This treatment was used to measure the total ecosystem CO_2 flux (i.e. both autotrophic and heterotrophic produced respiration combined).

b. a ‘soil’ treatment, which was identical to the ‘ecosystem’ treatment except that all surface vegetation had been removed in September 2003. Similar to Grogan et al. (2001), clipping was used to remove above ground vegetation in the ‘soil’ plots (including a shallow moss layer) leaving litter and plant roots in place to minimise soil disturbance. The ‘soil’ treatment plots were used to measure respired CO_2 in the absence of plants (including litter decomposition and that produced belowground that would be ascribed to plants e.g. rhizosphere respiration).

Each individual treatment plot measured 50 cm by 50 cm and was situated within a larger ‘buffer’ square of dimensions 1.5 m x 1.5 m allowing a 1 m break between each of the treatment squares. A porous blackout cover was placed over the ‘soil’ plots that allowed water but not sunlight to pass through when not in use. The ‘soil’ treatment plots were regularly gardened to remove any vegetation that appeared in them.

During the summer of 2005 lengths of PVC pipe (diameter 30 cm, height 20 cm) were inserted to at least 6 cm depth, to serve as collars on which to house respiration chambers. Closed dark respiration chambers were constructed from lengths of PVC pipe (diameter 30 cm, height 20 cm) with lids made from PVC sheets covered by reflective foil (to minimise heating effects within chambers). Two holes were drilled into opposite sides (top and bottom) of each respiration chamber to accommodate Quick couplings (Colder Products Company, USA) with which to attach a molecular sieve CO_2 sampling system (Hardie et al., 2005). On sampling occasions, the respiration chambers were attached to collars using a black rubber seal, which formed an air-tight bond. Air and soil temperatures were recorded during sampling periods using ‘Tinyview’ loggers (Gemini data loggers, Chichester, UK), and depth of water table relative to peat surface was measured manually on each sampling occasion from dip wells located adjacent to each chamber.

2.3. Sample collection and processing

For collection of respired CO_2, chamber covers were attached to each collar *via* the black rubber seal, followed by atmospheric CO_2 removal from each chamber headspace using a CO_2 scrubbing system (see Hardie et al. 2005 for design details). CO_2 removal took approximately one hour for each chamber, by which time the equivalent of at least 7 chamber volumes worth of headspace gas would have been scrubbed. After scrubbing, respired CO_2 was allowed to build up and concentrations monitored using an infrared gas analyser (IRGA; EGM-4, PP Systems, UK). When sufficient CO_2 had collected in the chamber, it was trapped using the molecular sieve sampling system. The sampling system was connected to each chamber in a closed loop; headspace gas was passed from the chamber into a water trap filled with a desiccant (Drierite, Alfa Aesar, Germany), followed by the IRGA for analysis of CO_2 concentration before finally being returned back to the chamber *via* a molecular sieve cartridge (MSC). CO_2 contained in the gas stream that passed through each MSC was trapped by the zeolite (Hardie et al., 2005).

We collected respired CO_2 from all treatment plots during the growing season when the water table was close to the peatland surface (August 2005) and again when the water table was several cm deeper (September 2005). In addition to respiration samples, CO_2 was collected from approximately 1 m above the vegetation canopy to characterise the radiocarbon signature of the contemporary atmosphere. Two atmospheric samples were collected, concurrent with the August and September respiration sampling. Approximately 7-10 ml of CO_2 was collected from each treatment plot (and the contemporary atmosphere), providing sufficient sample for both ^{14}C and ^{13}C analysis. Each MSC was returned to the NERC Radiocarbon Facility where sample CO_2 was recovered by heating (500 °C) followed by cryogenic purification on a vacuum line (Hardie et al., 2005). After the final respiration collection in September 2005, vegetation samples were taken from each of the treatment plots, placed into plastic bags and stored in a cooler. On return to the laboratory, vegetation was washed in distilled water and dried in a vacuum oven at 40 °C. Homogenised sub-samples were then combusted to CO_2 in sealed quartz tubes at 900 °C.

A sub-sample of CO_2 obtained from each of the respiration and vegetation samples was analysed for $^{13}C/^{12}C$ on a dual inlet isotope ratio mass spectrometer (VG Optima, Micromass, UK). Results are reported using the delta notation with $^{13}C/^{12}C$ variations relative to the international

standard Vienna Peedee belemnite (VPDB; Coplen, 1994) with isobaric molecule corrections adapted from Craig (1957). Further sub-samples were prepared as graphite targets using Fe/Zn reduction (Slota et al., 1987) and analysed for ^{14}C by AMS using the 5 MV tandem accelerator (Freeman et al., 2008) at the Scottish Universities Environmental Research Centre (SUERC). ^{14}C data are expressed as %Modern with samples having been normalised to a $\delta^{13}C$ of -25 ‰ (Stuiver and Polach, 1977). In keeping with international practice the results are expressed at the ± 1 σ level for overall analytical confidence.

2.4. Age determination

As a result of anthropogenic activities, the radiocarbon concentration of CO_2 in the atmosphere has undergone rapid variation over recent decades. Firstly, the burning of fossil fuels has released vast quantities of ^{14}C-free CO_2 to the atmosphere. Secondly, atmospheric testing of nuclear devices in the 1950s and early 1960s resulted in large quantities of $^{14}CO_2$ being produced that quickly mixed throughout the Earth's atmosphere. The result of these processes was to create a characteristic pattern of global atmospheric $^{14}CO_2$ concentration that initially exhibited a rapid increase from the mid-1950s to a peak in 1963, when a moratorium on atmospheric nuclear weapons testing came into force. This peak was followed by a progressive decline in the atmospheric concentration of $^{14}CO_2$ as it spread into other components of the carbon cycle and was further diluted by continued fossil carbon emissions. Living plants record the ^{14}C signature of the atmosphere from which they are formed. As a result of the rapid variation in the radiocarbon concentration of atmospheric CO_2, carbon derived from plant material that was fixed during the post-bomb period, can be dated accurately by comparing plant ^{14}C concentration with a record of atmospheric $^{14}CO_2$ e.g. Levin & Kromer (2004). In the present study, we determined the mean age of respired CO_2 using this approach in conjunction with the 'CaliBomb' calibration program (Reimer et al., 2004).

2.5. Isotope mass balance (two-component)

We initially partitioned ecosystem respiration into two sources based on a two-component mass balance model:

$$\mathbf{D_{eco} \times F_{eco} = (D_{soil} \times F_{soil}) + (D_{plant} \times F_{plant})} \quad \mathbf{(1)}$$

where D represents the isotopic concentration (either $\delta^{13}C$ or ^{14}C %Modern), and F the flux, i.e. the rate at which CO_2 was produced both in the absence of plants within the clipped 'soil' plots ($_{soil}$) and in the presence of plants ($_{plant}$); both these sources contributing to total ecosystem ($_{eco}$) CO_2 flux represented by the 'ecosystem' plots. We assumed that the difference in CO_2 flux and isotope measurements between our 'ecosystem' and 'soil' plots represented the plant source, and therefore:

$$\mathbf{F_{plant} = F_{eco} - F_{soil}} \quad \mathbf{(2)}$$

Two approaches were initially investigated using the above isotope mass balance equation. Firstly, we used the measured CO_2 flux rates from the 'ecosystem' and 'soil' plots to calculate the isotopic composition of plant respiration (D_{plant}). Secondly, utilising only the ^{14}C results and an assumption that plant respiration (D_{plant}) would be modern (i.e. with a %Modern identical to the contemporary atmosphere), we estimated the contribution of the plant source to total ecosystem CO_2 flux. The two-component mass balance model detailed above was subsequently found to be insufficient to describe our data and therefore, we put forth a three-component mass balance model. Further detail is given in the Results and Discussion, section 3.7.

2.6. Statistical analysis

All data were analysed using a one-way analysis of variance (ANOVA) to determine differences between treatments (for both flux and isotope data). *Post hoc* tests (Tukey HSD) were performed to elucidate differences between treatments on both sampling dates. All statistical analyses were carried out using the statistical software package Minitab (Release 15). All errors are reported to 1 significant figure unless the leading digit is a 1 or a 2, in keeping with standard practice in the reporting of uncertainties (Taylor, 1997).

3. Results and Discussion

3.1. ^{14}C and $\delta^{13}C$ of peatland vegetation and atmospheric CO_2

Carbon isotope results for peatland vegetation and atmospheric CO_2 are given in Table 1. ^{14}C concentrations of peatland ericoids and bryophytes sampled in September of 2005 ranged from 106.2 ± 0.3 %Modern to 107.5 ± 0.3 %Modern. There was no statistical difference in ^{14}C concentration ($P > 0.05$) between *Sphagnum capillifolium* and *Calluna vulgaris* shoots or the bryophyte *Hypnum jutlandicum* (which was the most enriched in ^{14}C of the four vegetation samples). The radiocarbon concentration of the atmosphere in August of 2005 (107.0 ± 0.3 %Modern) was slightly enriched relative to atmospheric CO_2 sampled in September of 2005 (106.0 ± 0.3 %Modern), but not significantly so ($P > 0.05$). All vegetation ^{14}C concentrations were statistically indistinguishable ($P > 0.05$) from the contemporary atmosphere. $\delta^{13}C$ values for *Calluna vulgaris* samples ranged from -27.5 to -27.8 ± 0.1 ‰ for flowers and shoots, respectively (Table 1). Samples of *Calluna vulgaris* were statistically more enriched ($P < 0.05$) in ^{13}C relative to *Hypnum* spp. and *Sphagnum* spp. samples that had $\delta^{13}C$ values of -30.5 and -30.4 ‰, respectively.

The ^{14}C concentration of peatland vegetation was measured to verify that vegetation was indeed representative of the contemporary atmosphere, and so to determine the ^{14}C concentration of inputs to the peatland carbon pool during the year of sampling. Several studies have suggested that peatland vegetation, such as *Sphagnum* recycles soil respired CO_2 based on stable (Price et al., 1997; Proctor et al., 1992) and radiocarbon analyses (Jungner et al., 1995; Turetsky and Wieder, 1999). Our results confirm that living vegetation at the study site had radiocarbon concentrations identical to that of the contemporary atmosphere; however, the ^{14}C results do not indicate whether any plant carbon was derived from the fixation of respired CO_2 because the ^{14}C concentration of ecosystem respiration was also found to be identical to the atmosphere. Thus, even if plant tissue contained a large proportion of carbon produced from respired CO_2, it would be unlikely to result in plant ^{14}C concentration being significantly different to the contemporary atmosphere.

3.2. CO_2 fluxes

Individual flux measurements for each treatment plot are given in Table 2, with average respiration fluxes produced by the 'soil' and 'ecosystem' treatments illustrated in Figure 1. Results for replicate 3 of the 'ecosystem' treatment (September) were eliminated as the flux measured from this plot was only 19 % of the mean flux of the remaining two 'ecosystem' plots in September and 22 % of the mean 'ecosystem' flux in August. Furthermore, the flux from this 'ecosystem' chamber was considerably lower than any of the 'soil' plots. The $\delta^{13}C$ value obtained for respired CO_2 collected from this treatment plot was 8.2 ‰ higher than the average $\delta^{13}C$ value obtained for the remaining two 'ecosystem' plots sampled on the same day (Table 2). The respiration sample produced by 'ecosystem' 3 for September was therefore deemed unreliable, as it seemed likely, given both the flux rate and the $\delta^{13}C$ value, that there was gross contamination from atmospheric CO_2. Furthermore, this sample was the only one collected when the water table extended to a depth below the base of the chamber collar (Table 2); all other chamber samples were unlikely to have significant air contamination as the water table would have formed a good seal with the base of the collar.

The 'ecosystem' treatment produced the highest CO_2 fluxes, with the largest average flux taking place in September (166.8 ± 1.9 mg C m^{-2} h^{-1}). A similar but smaller value (119 mg C m^{-2} h^{-1}) was reported for incubated peat monoliths (dominated by *Eriophorum vaginatum*) removed from a Swedish peatland (Strom et al., 2005), whereas fluxes emanating from a Finnish ombrotrophic low sedge bog were slightly higher at between 183-259 mg C m^{-2} h^{-1} (Silvola et al., 1996b). Average CO_2 fluxes produced by the 'soil' treatment in August were 53 ± 5 mg C m^{-2} h^{-1} and in September 60 ± 10 mg C m^{-2} h^{-1} (37 and 35 % respectively of those produced by the 'ecosystem' plots in the same months). The flux data were analysed statistically by a General Linear Model, which demonstrated that fluxes were significantly higher for the 'ecosystem' treatment relative to the 'soil' treatment ($P < 0.001$). Soil temperature at the site was a stable 11.5 °C on each of the sampling days in both August and September (under both treatments).

3.3. ^{14}C and $\delta^{13}C$ values of respired CO_2

Results for the carbon isotope composition of respired CO_2 produced by the two treatments in both August and September 2005 are given in Table 2 (with average ^{14}C data illustrated in Figure 2). The $\delta^{13}C$ of 'ecosystem' respired CO_2 (average) ranged between -20.8 ± 1.5 ‰ in August to -23.2 ± 0.6 ‰ in September. The $\delta^{13}C$ of respired CO_2 from the 'soil' treatment was depleted in ^{13}C relative to the 'ecosystem' treatment at -27.3 ± 0.6 ‰ in September to -27.4 ± 0.4 ‰ in August. The $\delta^{13}C$ of CO_2 from the 'soil' plots ranged between -26.8 ‰ and -28.0 ‰ and was very similar to values recorded for the *Calluna vulgaris* (Table 1) samples, and bulk peat collected from the top 16 cm of the site (Hardie et al., 2007). That the $\delta^{13}C$ of 'soil' CO_2 was similar to the underlying soil suggests there was very little contamination in the chamber from atmospheric CO_2, which we attribute to two factors. Firstly, to effective scrubbing of atmospheric CO_2 in chambers prior to CO_2 build up. Secondly, to minimal invasion of atmospheric CO_2 inside chambers during CO_2 build up and collection due to reliable seals that attached chambers to collars and, because the base of each collar extended to depths below the water table (Table 2).

The average ^{14}C concentration of the contemporary atmosphere for August and September of 2005 was 106.5 ± 0.7 %Modern and is given as a reference in Figure 2. The average ^{14}C content of 'ecosystem' respired CO_2 ranged between 107.0 ± 0.4 and 106.53 ± 0.13 %Modern and therefore was identical to the ^{14}C concentration of atmospheric CO_2. 'Soil' respired CO_2 was significantly ^{14}C-enriched relative to both the contemporary atmosphere and 'ecosystem' respiration (on both dates), ranging from 114.6 ± 0.4 %Modern in August, to 116.3 ± 0.4 %Modern in September. In addition, soil respired CO_2 produced in September was significantly enriched in radiocarbon ($P < 0.05$) relative to that produced in August. By comparison with a record of atmospheric $^{14}CO_2$ (Levin and Kromer, 2004), and assuming that all of the CO_2 respired from the 'soil' treatment plots was derived from carbon fixed since the peak of atmospheric $^{14}CO_2$ in 1963, we estimate that 'soil' respiration was derived from carbon that was originally fixed ~ 15 years prior to the time of sampling (see section 2.4. for further detail).

3.4. Partitioning ecosystem CO_2: two-component model

In this study we partition total ecosystem CO_2 by contrasting plots of intact vegetation ('ecosystem') with plots where vegetation had been removed ('soil' plots). We attempt to partition ecosystem produced CO_2 into contributions from 'plant' and 'soil' sources, but like all other techniques used for partitioning ecosystem CO_2 sources, our approach has caveats, and therefore what we mean by these CO_2 sources must be defined.

It is not possible to simply remove the plant contribution from ecosystem respiration without causing some other disturbance to the system. In our approach, clipping was used to remove plants and therefore isolate the heterotrophic 'soil' source of respiration. Plant roots were left in the soil because any attempt to remove them would have caused a level of disturbance we deemed unacceptable. Instead, it was considered that leaving the 'soil' plots two years between clipping and CO_2 collection would mean that most of the faster cycling plant carbon pools such as fine roots and root exudates would have considerably diminished, similar to that performed in other studies (Grogan et al., 2001; Ward et al., 2009). This approach inevitably resulted in the 'soil' plots not receiving the same fresh surface litter inputs as the 'ecosystem' plots for two years; however, had we performed the CO_2 collection directly after clipping, the 'soil' plots would have received a flush of nutrients from the decay of labile fractions, unlike the 'ecosystem' plots. It is difficult to quantify the effect of these two processes on the CO_2 efflux rate from the 'soil' plots and, for present purposes, we have assumed that the decrease in CO_2 efflux due to the absence of two years fresh litter would be approximately balanced by the increase in CO_2 emitted by the decay of residual roots and exudates. We have similarly assumed that these factors would not significantly influence the radiocarbon content of respiration, since the change in the radiocarbon concentration in the atmosphere and new carbon inputs would only have declined by less than 1 %Modern over two years between the establishment of the plots and sampling (Levin and Kromer, 2004).

The $\delta^{13}C$ of respired CO_2 from 'ecosystem' plots ranged between an average of -20.8 ‰ in August and -23.2 ‰ in September. As 'soil' respiration was ~ -27 ‰ for both months, the $\delta^{13}C$ values obtained for 'ecosystem' respiration indicate that when plants are present, the CO_2 emitted must contain a source of carbon that is enriched in ^{13}C. As the ^{14}C concentration of 'ecosystem' respiration (~ 107 %Modern) was identical to the ^{14}C concentration of the contemporary

atmosphere in both August and September 2005, and since 'ecosystem' respiration consists of both plant and soil respiration (the latter with a ^{14}C concentration of ~ 115 %Modern), it is immediately apparent that either plant respired CO_2 contained a source depleted in radiocarbon, or that the 'soil' contribution to total 'ecosystem' respiration was extremely small.

A two-component mass balance model (equation 1) was applied to the $\delta^{13}C$ and ^{14}C data obtained for both treatments; the flux of plant respiration was calculated by deducting the 'soil' flux from the 'ecosystem' flux. The $\delta^{13}C$ values for plant respired CO_2 calculated by mass balance were -16.9 ‰ in August and -20.9 ‰ in September. Mass balance revealed plant respired CO_2 to have a ^{14}C concentration of 102.3 %Modern in August and 101.4 %Modern in September. Peatland plants would not respire CO_2 with a ^{14}C signature of between 101 and 102 %Modern, as this would mean that plants were respiring carbon that was fixed before the peak in bomb-^{14}C of ~ 1963; furthermore, the calculated $\delta^{13}C$ values for plant respiration are much higher than values reported in the literature for C_3 plants (Boutton, 1991).

The above calculations assume that respiration produced by the bulk peat under the 'soil' treatment is exactly the same in the 'ecosystem' plots, but as discussed earlier, there are limitations to this approach. However, for the 'ecosystem' treatment to contain no pre-bomb component whatsoever, the 'soil' contribution to the total respired CO_2 flux would have to be less than 15 %. As the actual flux measured in the 'soil' treatment was ~ 36 % of the total 'ecosystem' flux, it is unlikely that, with the presence of plants, the flux from the soil in the 'ecosystem' plots would be less than this. Furthermore, even if we allow for a small amount of atmospheric CO_2 in the 'ecosystem' respiration chambers, and correct for this using the $\delta^{13}C$ values (e.g. Gaudinski et al. 2000) to estimate the air fraction, the results still imply a source of pre-bomb carbon present in 'ecosystem'-respired CO_2.

Alternatively, using a variation of the two-component mass balance equation, we can assume that plant respiration has a radiocarbon concentration similar to that of the contemporary atmosphere, as also done by Gaudinski et al. (2000), and calculate the fraction that plant respiration contributes to 'ecosystem' respiration independently of the flux measurements. The two-component mass balance equation (equation 1) is adapted for ^{14}C (Δ) values as:

$$\Delta_E = \Delta_P F_P + \Delta_S(1 - F_P) \quad (3)$$

where F_P is the flux fraction that is plant respiration and $(1 - F_P)$ is the fraction that is soil respiration. Substituting the ^{14}C data for August into equation 3 gives $F_P = \sim 1.0$, i.e. that plant respiration contributes 100 % of total ecosystem respiration, and therefore, there is no contribution from 'soil' respiration. Similar results are obtained for September with 'plant' and 'soil' sources calculated to contribute 94.7 and 5.3 %, respectively. Again, as the calculated soil respiration fraction is far less than the actual fluxes produced by the 'soil' plots (36 % of 'ecosystem' respiration), it appears once again, that the two-component mass balance model fails to describe the system under examination. Therefore, we postulate the presence of a third contribution to ecosystem respired CO_2 and suggest that this third source is mediated by the presence of plants, i.e. only occurs when plants are present.

3.5. Partitioning ecosystem CO_2: three-component model

We defined a flux and isotope value for each potential source: i.e. plant respiration (flux F_P, Δ_P, δ_P), soil respiration (flux F_S, Δ_S, δ_S) and additionally, a flux and isotope contribution produced by the presence of plants (flux F_C, Δ_C, δ_C). Mass balance was applied to the entire system followed by isotope balance i.e. (flux F_E, Δ_E, δ_E), as follows:

$$F_E = F_P + F_S + F_C \quad (4)$$

where F is the fraction of the flux that each pool contributes to the total (F_E), and $F_E = 1$.

$$\delta_E F_E = \delta_P F_P + \delta_S F_S + \delta_C F_C \quad (5)$$

where δ is the stable carbon isotope composition of CO_2; and

$$\Delta_E F_E = \Delta_P F_P + \Delta_S F_S + \Delta_C F_C \quad (6)$$

where Δ is the radiocarbon concentration of respired CO_2. Since $F_E = 1$ we can express equation 4 as:

$$F_C = (1 - F_P - F_S) \quad (7)$$

The fraction of the third source F_C is then substituted in equations 5 and 6, giving:

$$\delta_E = F_P(\delta_P - \delta_C) + F_S(\delta_S - \delta_C) + \delta_C \quad (8)$$

and:

$$\Delta_E = F_P(\Delta_P - \Delta_C) + F_S(\Delta_S - \Delta_C) + \Delta_C \quad (9)$$

We have measured the values for Δ_E, Δ_S, δ_E and δ_S but we must make some assumptions about Δ_P and δ_P as they were not measured directly. First, we assume that Δ_P has the same ^{14}C concentration as the contemporary atmosphere (Gaudinski et al., 2000; Schuur and Trumbore, 2006) on the same date that Δ_S and Δ_E were measured in August and September of 2005. In addition, a value of -27 ‰ is assumed for the $\delta^{13}C$ of plant respiration (Gaudinski et al., 2000). The chosen values for δ_P and Δ_P and the measured carbon isotope values (for August) are substituted into equations 8 and 9, and rearranged:

$$F_P = (10.66 + 0.63\delta_C) / (27 + \delta_C) \quad (10)$$

$$63.27 = F_P(106.98 - \Delta_C) + 0.63\Delta_C \quad (11)$$

Therefore, substituting equation 10 for F_P in 11 gives:

$$63.27 = 0.63\Delta_C + ((10.66 + 0.63\delta_C) / (27 + \delta_C))(106.98 - \Delta_C) \quad (12)$$

The only unknowns in equation 12 are δ_C and Δ_C, the stable carbon and radiocarbon compositions of the postulated third pool, the two quantities that we require. Although we cannot derive unique values from equation 12, we can model the locus of pairs (δ_C, Δ_C) that satisfy the equation. Calculated pairs of Δ_C and δ_C that satisfy equation 12 are illustrated in Figure 3 for both August and September.. In addition, a full error propagation has been executed for all measured parameters present in equation 12; thus giving an estimate of error for the modelled $\delta^{13}C$ and ^{14}C values of the third source (error bars, Figure 3). Calculated points are constrained by the fact that the fraction of CO_2 contributed to the total by the third pool is unlikely to have a $\delta^{13}C$ value greater

than +20 ‰ (Scott et al., 1994). Figure 3 shows that the postulated third source of carbon could contribute between 13 and 63 % of the total 'ecosystem' CO_2 flux in August and between 8 and 65 % of the total flux measured in September.

It should be noted here that there is evidence emerging in the literature demonstrating that the $\delta^{13}C$ of foliar respired CO_2 is enriched in ^{13}C (up to several per mil) relative to both bulk plant tissue and substrates utilised for respiration (Duranceau et al., 1999; Duranceau et al., 2001; Ghashghaie et al., 2003; Ghashghaie et al., 2001; Tcherkez et al., 2003; Xu et al., 2004). However, many of these studies show that fractionation of ^{13}C is most pronounced under drought conditions or elevated temperatures e.g. up to 35 °C for the study by Tcherkez et al. (2003), neither of which environmental conditions are often appropriate for peatland plants at our site. In addition, Klumpp et al. (2005) point out that for respired CO_2 produced by the whole plant (i.e. including root and shoot respiration in addition to foliar or foliar substrate respiration) fractionation of ^{13}C in respired CO_2 is much less (between 0.4 and 0.9 ‰). However, even taking a 3 per mil fractionation into account and modelling our results using -24 ‰ as the chosen value for the $\delta^{13}C$ of plant respired CO_2, a third source depleted in ^{14}C but enriched in ^{13}C must still be invoked (although the contribution this source makes to the total ecosystem CO_2 flux is smaller).

Before estimating the size and the isotopic ($\delta^{13}C$ and ^{14}C) composition of the third pool of carbon, we must present a plausible suggestion as to the source of the third carbon pool. Peatland vegetation holds the key to the third pool of carbon, as it is when vegetation is present that the derived values from the two-component mass balance equation are either not consistent with what was measured (flux rates) or seem unrealistic (plants respiring pre-bomb peak carbon).

It is well established in the literature that certain peatland plants, in particular vascular plants such as grasses and sedges (e.g. *Eriophorum, Carex* and *Juncus*), serve as conduits for the transport of methane from depth to the atmosphere (Chanton et al., 2005; Chanton et al., 2002; Chanton and Whiting, 1995; Marinier et al., 2004; Rinnan et al., 2003; Schutz et al., 1991; Shannon et al., 1996; Strom et al., 2005; Verville et al., 1998; Watson et al., 1997). The development of aerenchymateous tissue in vascular plants is thought to have arisen due to soil anoxia, and provides the submerged parts of plants with oxygen. Indeed, the transfer of O_2 to depth, and its subsequent consumption, causes gases present in and around the root zone to flow to the atmosphere. In so

doing, this process has been shown to cause pressure deficits of up to 20 % in the root zone (the concentration of O_2 in the atmosphere) (Piao et al., 2007; Raskin and Kende, 1983; 1985). In another study, Koncalová et al. (1988) showed movement of gas from plant roots to the atmosphere (*via* non-through-flow convection), whilst facilitating O_2 transport to depth. Finally, Joabsson et al. (1999) maintain that one mechanism of bulk transport of gases from peat to the atmosphere, thermo-osmosis, results in the flushing of 'methane and other gases accumulated in the root zone'.

Whilst the majority of the aforementioned studies have been concerned with methane, it is very likely that, whatever the mechanism, the transport of gases from the root zone is also an important pathway for CO_2 release. Indeed, in a recent literature review on gas transport in plants, Colmer (2003) says 'Aerenchyma provide a low-resistance internal pathway for gas transport between shoot and root extremities. By this pathway, O_2 is supplied to the roots and rhizosphere, while CO_2, ethylene, and methane move from the soil to the shoots and atmosphere'. This is particularly true for wetland plants such as sedges e.g. *Carex*. Furthermore, *Eriophorum vaginatum*, the dominant monocotyledon vascular plant at the Hard Hill site, can produce roots that penetrate up to 1 m into the peat profile (Heal et al., 1978). This being the case, older CO_2, existing at depth within a peat bog (in addition to CH_4), will be transported to the atmosphere with the assistance of this type of vascular plant. In addition to transport through plant aerenchyma, mechanisms such as diffusion and CH_4 ebullition will also participate in the release of CO_2 from depth within a peat bog. It should also be mentioned here, that when CH_4 is transported to the atmosphere from depth in a peat bog *via* the aerenchyma of plants, it escapes oxidation by methanotrophs. There is no such removal mechanism for CO_2 and therefore the mechanism of transport from depth to the surface will have little effect on the overall flux of CO_2 from depth to the atmosphere.

However, unless the proposed third source is quite sizeable, concomitant $\delta^{13}C$ values must be much higher than those found in the surrounding bulk peat (see Figure 3). This source (in addition to being depleted in ^{14}C) should contain CO_2 that is sufficiently enriched in ^{13}C as to produce positive $\delta^{13}C$ values. Enriched $\delta^{13}C$ values for CO_2 at depth within peat profiles have been reported. For example, Charman et al. (1999) measured the stable carbon isotope composition of deep carbon gases in an English raised mire and found CO_2 that was particularly ^{13}C-enriched with

$\delta^{13}C$ values of up to +7.1 ‰ (at depths of 2.3 to 2.5 m). In a Scottish study of deep peat methane stable carbon isotope ratios, Waldron et al. (1999) measured accompanying $\delta^{13}C$-CO_2 values of up to +9.6 ‰ at depths of 3 m. Finally, and most recently, Clymo & Bryant (2008), in a study of deep peat gases in a Scottish raised peat bog recorded $\delta^{13}C$ values of between +4.0 ‰ and +10.0 ‰ at depths of 1.5 to 6 m.

The aforementioned studies suggest that ^{13}C-enriched CO_2 was formed during methanogenesis (a process that produces CH_4 that is highly depleted in ^{13}C and ^{13}C-enriched CO_2), either by acetate fermentation (Clymo and Bryant, 2008) or CO_2 reduction. Therefore, the range of $\delta^{13}C$ values predicted by our models of locus pairs is realistic. Furthermore, the predicted age of our third source is also easily possible and indeed the mineralisation of very old soil organic carbon has been demonstrated recently (Fontaine et al., 2007) in a soil-priming experiment. The latter study showed that following addition of cellulose, microbes were stimulated into breaking down a soil organic carbon pool (60-80 cm depth) that had an age of 2,567 ± 226 years BP. Accordingly, we believe that the supply of fresh organic material (recently fixed) translocated below-ground by the aerenchyma of peatland vascular plants (in addition to the transfer of O_2) stimulates the microbial breakdown of old organic carbon, whilst simultaneously transferring gases from depth to the atmosphere. It is clear then, that CO_2 released from the catotelm (the permanently waterlogged and anoxic layer of a peatland), facilitated by plants, could be enriched in ^{13}C whilst at the same time being depleted in ^{14}C

Studies have shown that the rate of input to the catotelm from the acrotelm (the surface layer of a peatland where fluctuation of the water table occurs) is about 10 % of primary productivity (Clymo, 1983; Schimel, 1995; Tolonen et al., 1992). According to Clymo (1984), the accumulation rate in the acrotelm at a nearby study site, also within Moor House National Nature Reserve, is 450 g m^{-2} yr^{-1}; accordingly the rate of organic matter input to the catotelm is about 45 g m^{-2} yr^{-1}. If we make the simplifying assumption that net carbon accumulation is close to zero in the catotelm, i.e. that the peatland has reached its limit of growth (Clymo, 1984), the rate of input to the catotelm from the acrotelm must be balanced by an output from the catotelm of ~ 45 g m^{-2} yr^{-1} (as CO_2, assuming loss *via* dissolved organic carbon and CH_4 is minimal). If we also assume that

the vast majority of catotelm CO_2 lost from the peatland is mediated by plants, then the postulated third pool of carbon would be approximately equal to the loss of CO_2 from the catotelm and therefore be ~ 45 g m^{-2} yr^{-1}. This flux expressed as a proportion of the total soil-derived (i.e. exclusive of plant respiration) CO_2 is ~ 10 %. Clearly, due to the assumptions used in the above calculations, the estimate that catotelm CO_2 could contribute ~ 10 % of total soil-derived CO_2 must be treated with caution. However, it does serve to illustrate the possibility of a plant-mediated catotelm CO_2 flux of similar magnitude to that implied by our three-box model.

From the three-box models for August and September featured in Figure 3 we can estimate that when plants are present, the contribution to total 'ecosystem' flux from catotelm CO_2, would be in the region of ~ 10-23 % (assuming a $\delta^{13}C$ of between 0 and +10 ‰ for catotelm CO_2, and therefore a ^{14}C content of between 77.8 to 89.6 %Modern, i.e. ^{14}C age of 882 and 2017 years BP). Therefore, the total soil-derived CO_2 contribution to the 'ecosystem' CO_2 flux would be between 46 and 59 % (~36 % that was measured in the 'soil' plots plus 10-23 % catotelm CO_2). Plant-mediated catotelm CO_2 would then contribute a relatively large fraction of total soil-derived CO_2 flux (22-39 %), between 2 to 4 times that calculated (for catotelm CO_2) above using the data from Clymo (1984). The difference may not be surprising, as the estimate calculated for the catotelm CO_2 contribution using the Clymo (1984) data is an annual estimate. The estimate calculated here is based on rates measured during the growing season months of August and September when plant activity is at its highest; this could result in an increased conduit effect and consequently a greater soil priming effect (Kuzyakov et al., 2000).

4. Conclusions

'Soil' respiration was found to contribute ~ 36 % of total ecosystem respiration and maintained a relatively small range in radiocarbon signatures (between 114.6 and 116.3 %Modern) across the three sampling plots. Based on the bomb-^{14}C content, 'soil' respired CO_2 had originally been fixed, on average, 15 years prior to sampling, whereas ecosystem respiration had a ^{14}C content that was indistinguishable from the contemporary atmosphere. Isotope mass balance revealed there to be a source other than 'soil' and 'plant' respired CO_2 contributing to total ecosystem CO_2 flux. Modelling of locus pairs suggested that this third source (plant-mediated catotelm CO_2) was both

depleted in ^{14}C whilst being enriched in ^{13}C, and that this source could contribute a sizeable flux of CO_2 to the atmosphere (perhaps between 10-23 % of the total peatland ecosystem CO_2 flux).

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Table 1

Publication Code (SUERC-)	Sample Identifier	^{14}C Enrichment (%Modern ± 1 σ)	$\delta^{13}C_{VPDB}$ (‰) ± 0.1
8516	*Calluna vulgaris* shoots	106.2 ± 0.3	-27.8
8517	*Calluna vulgaris* flowers	106.6 ± 0.3	-27.5
8518	*Hypnum jutlandicum*	107.5 ± 0.3	-30.5
8520	*Sphagnum capillifolium*	106.5 ± 0.3	-30.4
8115	Atmospheric CO_2 - August	107.0 ± 0.3	-8.9
8124	Atmospheric CO_2 - September	106.0 ± 0.3	-8.8

Table 1 - ^{14}C and $\delta^{13}C$ values of peatland vegetation and atmospheric CO_2 in 2005. Atmospheric CO_2 was collected from 1 m above the peatland surface. 1 σ = 1 standard deviation.

Table 2

Publication Code (SUERC-)	Sample Identifier	^{14}C Enrichment (%Modern ± 1 σ)	$\delta^{13}C_{VPDB}$ (‰) ± 0.1	CO_2 Flux mg C m^{-2} h^{-1}	Base of chamber collar (cm)	Water table depth (cm)
8109	Eco 1 – August	107.1 ± 0.3	-22.5	157.2	7.9	5.5
8110	Eco 2 – August	107.3 ± 0.3	-20.3	142.2	7.1	-0.1
8111	Eco 3 – August	106.5 ± 0.3	-19.7	130.5	6.3	3.9
8112	Soil 1 – August	114.6 ± 0.4	-27.1	52.0	8.3	2.7
8113	Soil 2 – August	115.1 ± 0.4	-27.8	47.3	10.7	-0.1
8114	Soil 3 – August	115.1 ± 0.4	-27.4	58.2	10.9	2.8
8115	Atmos – August	107.0 ± 0.3	-8.9	-	-	-
8116	Eco 1 – September	106.4 ± 0.3	-23.6	165.5	7.9	7.1
8119	Eco 2 – September	106.6 ± 0.3	-22.8	168.1	7.1	5.4
8120	Eco 3 – September	107.9 ± 0.3	-15.0	30.9	6.3	6.7
8121	Soil 1 – September	115.9 ± 0.4	-26.8	69.1	8.3	3.5
8122	Soil 2 – September	115.9 ± 0.4	-28.0	64.7	10.7	5.1
8123	Soil 3 – September	116.3 ± 0.3	-27.1	42.5	10.9	8.1
8124	Atmos – September	106.0 ± 0.3	-8.8	-	-	-

Table 2 - ^{14}C, $\delta^{13}C$ and flux of respired CO_2 from treatment plots. Also given are depths to the base of each individual chamber collar and water table depth, both relative to the peatland surface (August and September 2005). 1 σ = 1 standard deviation. The column entitled 'Sample Identifier' gives the treatment (Eco = 'ecosystem' and Soil = 'soil'), replicate number, and month of sample collection. Atmos = atmosphere sampled on the same day as treatment plots.

Figure captions:

Figure 1 - Mean respiration fluxes measured in August and September 2005. n = 3 except for September where n = 2 for the 'ecosystem' treatment. Error bars are 1 standard deviation.

Figure 2 - ^{14}C concentration of respired CO_2 produced by both treatments in August and September 2005. Atmospheric $^{14}CO_2$ concentration is given as a dashed line with ± 1 σ confidence interval. n = 3, except for the 'ecosystem' treatment in September where n = 2. Error bars are 1 standard deviation.

Figure 3 - Plot illustrating carbon isotope values for the third CO_2 source (δ_C and Δ_C) that fit the model predicted by equation 12 for August (also illustrated are the equivalent values determined for September). Numbers with arrows show the fraction of the total flux that could be attributed to the third source given the set of locus pairs. Values illustrated are possible based on the fact that the flux of the third source must be a fraction ≤ 0.65 of the total flux and in addition is unlikely to have a $\delta^{13}C$ value greater than +20 ‰. Error bars for modelled $\delta^{13}C$ and ^{14}C values are based on a full error propagation of all measured parameters used in equation 12.