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Original Research Article

Carbon dioxide measurement in Irish blanket peatlands:
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ABSTRACT

Peatlands have been recognised as having a significant role in the mediation of atmospheric carbon dioxide (CO₂) levels with direct implications for global climate change. Longitudinal in situ measurement systems for CO₂ concentrations in blanket peatland ecosystems are difficult to implement where the nature of terrestrial-aquatic connectivity and hydrodynamics have a significant effect on the carbon cycle. The need for greater data on CO₂ concentrations and flux monitoring in these settings has been well recognised. However, applying the most appropriate monitoring approach presents a special challenge. This paper sets out the development of a direct method for field based longitudinal CO₂ concentration measurement. Based on experiential considerations a new approach is presented that addresses the complexity associated with the high diurnal dynamics of CO₂ evasion during mid-winter in an Irish blanket peatland soil–water system. The paper outlines the significance of a direct in situ continuous measurement strategy using a non-dispersive infrared (NDIR) sensor to evaluate CO₂ concentrations. The CO₂ concentrations recorded as part of this study showed significant differences between the pond waters and the peat waters. The overall CO₂ concentration trend did not correlate with the temperature patterns. Further monitoring is essential to evaluate the spatial and longitudinal trends in carbon dynamics. Outputs of this study will have a direct bearing on approaches to carbon flux determinations for this landscape type and will provide an important input to future efforts to explore carbon-hydrodynamics in the surface and sub-surface waters of blanket peatlands.

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1. Introduction

1.1. Blanket peatlands and hydrodynamics

Peat is a biogenic deposit which has predominantly developed in the current interglacial period of the Holocene

(Hammond, 1981). Peat accumulates under conditions of impeded drainage and O₂ (oxygen) deficiency in areas where the rate of plant production exceeds the rate of plant decomposition (Feehan and O'Donovan, 1996). Peatlands are a type of terrestrial wetland ecosystem that arises where land areas are saturated with water and precipitation inundation is sufficient in frequency and duration to support the ecosystem's unique vegetation (Otte, 2003). It has been estimated that there are about 4.5 million km² of peatland globally (Amundson, 2001; Otte, 2003; Schulze and Freibauer, 2005; Bullock et al., 2012; Turner et al.,

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2013). These peat deposits are storing approximately 400 billion tons of peat which represents between one-third and one-half of the world's soil carbon pool (Amundson, 2001; Otte, 2003; Holden, 2005; Schulze and Freibauer, 2005; Bullock et al., 2012; Turner et al., 2013). The scale and long-term ability of these peatlands to store carbon and mediate CO₂ levels within the atmosphere represents a crucial component in global climatic biosphere feedback systems and hence underscores the importance of understanding the volumes and pathways of carbon dynamics and CO₂ efflux arising from these soil-ecosystems. However, global estimates of the annual net release of CO₂ from this soil-ecosystem landscape component remains uncertain particularly when compared to other elements in the global carbon budget (Le Quéré et al., 2009).

Given the scale and dynamics of water within the peatland ecosystems it is not surprising that much of the evasion of carbon in these ecosystems is mediated by hydro-dynamic processes including the translocation of dissolved CO₂, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and the rate and location of CO₂ diffusion (Raymond et al., 2013; Leith et al., 2015). This study explores the contribution of CO₂ evasion from the lentic waters and soils of blanket peatlands. Blanket bogs initially develop in discrete locations which ultimately coalesce into a widespread peat landscape ranging in depth from 2 to 8 m (Feehan and O'Donovan, 1996). In general, this peat type follows the underlying topography except on very steep slopes. The stratigraphy of these peatlands is typically considered with reference to the diplotelmic system which comprises an upper, periodically aerated, and partly living soil layer (acrotelm) and a lower anaerobic layer (catotelm) where metabolic activity is greatly reduced (Holden and Burt, 2003). The general flow pattern of water in these peatlands is horizontal on or near the surface and through the upper layers of peat at the top of the water table (Lindsay, 1995). This flow pattern is highly variable and often produces surface ponds and hollows where water movement is greatly reduced. Flow in the catotelm is much less and is often characterised as minor in terms of contributions to overall flow (Lindsay, 1995). However, the existence of larger matrix channels, macropores and soil pipes within the catotelm means that a significant portion of water transport in blanket peats can be quite rapid even in deeper peat layers. Soil-water CO₂ efflux is a major component of the biosphere's carbon cycle and has been estimated to contribute up to three-quarters of total ecosystem respiration (Law et al., 2002). This underscores the importance of understanding the nature and source of CO₂ generation in this significant ecosystem type.

1.2. Water–CO₂ evasion in blanket peatlands

A major issue for water quality control in recent years has been the rising trend in the concentration of DOC from peatland catchments. The doubling of levels of DOC (and the associated discolouration of water) has been identified as one of the single largest changes in upland water quality (Worrall et al., 2003; Labadz et al., 2010). Indeed, the transport of carbon through the labyrinth of hydraulic pathways that characterise blanket peatland settings

represents a significant component affecting regional carbon balances including the efflux of CO₂ into the atmosphere (Dinsmore et al., 2011; Fasching et al., 2014; Yang et al., 2015; Ruhala and Zarnetske, 2017). Since water is strongly associated with the control and transport of carbon (organic and inorganic; dissolved and particulate) it is important to understand the associated hydrodynamics of these systems (Wallin et al., 2011, 2013; Whitfield et al., 2011). As the sources of CO₂ vary in space and time, measurement of CO₂ concentrations in peatland surface water systems represents a key contribution to overall carbon cycle determinations. Measurements in this area are of interest to researchers from a range of disciplines concerned with the biogeochemistry, ecology and hydrology of wetlands, ponds, streams and lakes (Battin et al., 2008; Bodmer et al., 2016). It is also a parameter of interest in addressing questions on the terrestrial–aquatic connectivity of groundwater and surface water and the carbon cycle in general (Cole et al., 2007).

1.3. Approaches to the measurement and monitoring of CO₂ in peatlands

The longitudinal evaluation of CO₂ dynamics in the waters within the lentic–lotic continuum of peatland settings is problematic. The ephemeral and intermittent nature of ponds, pools and streams that flow in rills and gullies across the peatland landscape coupled with the high variability in water flow rates within peatland ecosystems makes long term monitoring of dissolved CO₂ patterns a precarious endeavour. Various approaches have been applied over the years to evaluate the efflux of CO₂ from freshwater systems. However, efforts have been largely limited to either making spot measurements based on direct extraction and testing (Kling et al., 1991; Hope et al., 1995) or based on indirect estimates of the dissolved CO₂ concentration from measurements of other parameters including pH and alkalinity (Neal et al., 1998). Johnson et al. (2010) set out a new approach to the continuous direct in situ measurement of CO₂ efflux from freshwaters using an infra-red gas analysis. The non-dispersive infra-red (NDIR) sensor technique has, in one form or another, been in use since the 1930s (Choi and Son, 2011). However, changes in the application systems, including power source, probe size, etc. now mean that it is possible to utilise this technique in remote settings. This study has sought to address the challenge of the long-term measurement of peatland CO₂ efflux values through the development of a robust and adaptive installation system using NDIR technologies sampling pools and the waters of the peat soil immediately adjacent to the pools. The set-up proposes a unique installation for the soil water probes that affords high dynamic flexibility with variation in water table depth and a site monitoring configuration targeting a profile of the micro habitats.

2. Materials and methods

2.1. The study site

The study area was in an extensive upland blanket peatland area within the Wicklow Mountains, County

Wicklow, Ireland. This blanket peatland represents a significant mire ecosystem ranging from 15 to 30 km in width and stretching for more than 40 km in a north–south direction (Fig. 1) (Aalen et al., 2011). This study was located on Liffey Head Bog which is located within the Wicklow Mountains National Park one of the largest national parks in Ireland. This upland blanket peatland is a site of international importance and a conservation area managed by the Irish National Parks and Wildlife Service (National Parks and Wildlife Service, 2017). It is an actively growing peatland and it has numerous pools and hollow microforms which are inhabited by a wide range of organisms (Conaghan et al., 2000). Pools within these peatland ecosystems are typically characterised as environments with greater organic carbon production than microbial mineralisation (Uhlmann et al., 2011). The perennial nature of these pools and the prevalence of slow and incomplete decomposition processes are favoured under surplus water availability from the atmosphere (precipitation) and from the surrounding terrestrial zone (run-off) coupled with low oxygen availability – an environment which should lead to net carbon sequestration, net peat accumulation and siltation (Uhlmann et al., 2011).

Within the Wicklow Mountains and the Liffey Head bog a suitable study site was selected on the interfluvium of the valleys of the adjacent headwaters, i.e. the dividing region between the catchments of the Dargle River, the Liffey River and the Cloghoge River (Fig. 1). This interfluvium has an approximate width of 200 m. The precise location (53°09.181'N, 06°16.988'W) was selected based

on parameters such as micro-topography, including a regular hummock–hollow–pool profile, and hydromorphological characteristics deemed representative of the wider peatland ecosystem in the region. The selection of these contrasting micro-characteristics is consistent with the approach advocated by Claire Horner-Devine et al. (2003). The study was undertaken over a three-week period in December 2016 to establish mid-winter values for this component of the CO₂ carbon cycle in these peatlands. The blanket peatland at the study site is positioned on porphyritic granite and the peat depth ranges from approximately 2.7 to 5 m in this region (Hannigan et al., 2011). The mean annual precipitation in the area can reach 2000 mm per annum (Met Eireann, 2017a) and the mean monthly temperature values reported for this region of Ireland range for 2–20 °C throughout the year (Sweeney, 2014) although microclimatic conditions clearly exist within the Wicklow Mountains and these values will be reduced with altitude.

The peat soil zone was selected as a transition zone between high lawn and low hummock vegetation (Johnson and Damman, 1991; Laiho, 2006). The pools at the study site exhibited characteristic dystrophic properties including the paucity of nutrients and calcium, high acidity and elevated concentrations of dissolved humic materials as typically reported by Uhlmann et al. (2011). The pool waters were clear but overall the pools presented as brownish in colour (Fig. 2). The peat pool area was approximately 100 m² and had depth of about 1.4 m although the boundary of a distinct pool bed is difficult to define given the existence of large amounts of soft detrital material (Fig. 2).

Fig. 1. The location of the study site – east coast of Ireland. Adapted from OSI (2017).

Fig. 2. The CO₂ 'Peat-Hydro' monitoring site in the Wicklow Mountains, Ireland.

2.2. Continuous in situ CO₂ efflux measurement

This approach has been adopted and adapted to the measurement of CO₂ concentrations arising from the freshwaters of the blanket peatland pools and the surrounding terrestrial zone. In this study, the sensor of choice was a Vaisala GMM220 CARBOCAP non-dispersive infra-red (NDIR) gas sensor (Fig. 3) (Vaisala, 2012, 2013). Other parameters recorded at the site during the measurement period included water, soil and air temperature and the atmospheric pressure.

The concentration of CO₂ is detected when infrared (IR) radiation is emitted from a light source and passes through the sample chamber to the detector – the variation in light intensity is detected and converted into a concentration value (Vaisala, 2012). This system offers several advantages compared to other spectroscopic techniques,

Fig. 3. The Vaisala GMM220 (GMP221 probe model) CARBOCAP sensor.

including the relatively low power consumption (<2.5 W) and its ability to operate at low temperatures (e.g. -20 °C) (Vaisala, 2013). However, there are some limitations, such as interference and detection limit (e.g. 0–10% or up to 100,000 ppm CO₂) which may require multiple units where the range to be covered is large (Vaisala, 2013). The Vaisala sensors are shipped with certificates of calibration (Johnson et al., 2010). The checked accuracy of this GMM220 NDIR sensor at 25 °C and 1012 hPa is $\pm 1.5\%$ of range $+2\%$ of reading (applies for concentrations above 2% of full scale) (Vaisala, 2013). For assessing the accuracy of the sensors after the field exposure, it is appropriate to use the 'field check adapter' which is a chamber for pump-aspirated sampling systems which can be used with calibration gases (Johnson et al., 2010). There is a consistent difference between the individual sensors and standard gases, but these can be illuminated by applying a sensor-specific linear correction factor (Johnson et al., 2010). It also has a short warm-up time of 30 s (15 min – full specifications) and response time of 20 s (Vaisala, 2013). Johnson et al. (2010) reported the transfer coefficient k_a and diffusivity D of the expanded PTFE membrane for CO₂ to be 0.8 ± 0.1 cm s⁻¹ and 0.08 ± 0.01 cm² s⁻¹, respectively. Since diffusion of CO₂ in water is about 10,000 times slower than in air the material diffusivity of the PTFE tubing and its transfer coefficient indicate that it presents a negligible barrier to CO₂ diffusion and the temporal response of the sensor (Johnson et al., 2010; Scott, 2000). Furthermore the use of the Vaisala sensor has shown high adaptability for robust field applications having been used in a number of lotic environments (Crawford et al., 2014).

The GMM220 sensor type that was used in this study was supplied with DC power (2×75 Ah, 12 V DC batteries deployed in-parallel) (Fig. 4) and the output was recorded with a data acquisition system (Vaisala data-logger; DL4000) (Fig. 4). The sampling interval was every minute. A digital timer was integrated into the circuitry to cycle the sensor on and off for measurements at a reduced frequency to conserve power and enable the system to operate for longer periods in the field before requiring a battery change.

Fig. 4. Equipment used in the study: (a) the battery set-up using 2×75 Ah, 12 V DC; and (b) the Vaisala DL4000 data-logger.

2.3. Pool and peat zone sensor installation

The Vaisala GMM220 NDIR sensor probes are approximately 20 mm in diameter by 150 mm long. These sensors are not suitable for direct deployment in aqueous solutions and need to be modified. The modification consists of using a protective expanded polytetrafluoroethylene (PTFE) tube sleeve that is highly permeable to CO_2 but impermeable to water. The PTFE sleeves were sealed using Plasti Dip rubberising compound which makes both the cable end and non-cable end of the sensors impermeable to water (Fig. 5).

Fig. 5. The Vaisala GMM220 NDIR sensor probe with the PTFE membrane attached.

The pool sensor was fixed inside and in line with the long axis of a perforated 500 mm $\times$ 100 mm PVC pipe. A mesh was then attached to the bottom end of the PVC pipe in to protect the sensor and PTFE sleeve from any potential impact damage from debris when in the field setting. The pool sensor and its protective PVC pipe were then secured in the middle of the pool with floats to ensure that the probe sat vertically and was held at a constant depth within the water (Fig. 6).

The peat soil conditioned sensor was similarly attached in line with the long axis of a perforated PVC pipe although in this case the pipe was longer (1000 mm $\times$ 100 mm). In this soil-based installation the perforated PVC pipe was fixed in the peatland. A float was attached to the top section of the sensor housing which is free to move independently inside the PVC pipe and the power and data leads were coiled within the upper sections of the pipe (Fig. 6). This procedure was developed to ensure that should the water level inside the PVC pipe change, the sensor assembly would move freely up and down inside the protective perforated PVC piping and so maintain a constant depth with reference to the water table of the peat. This sensor unit was placed in an 800 mm deep well excavated in the peat using an Edelman auger. The top 200 mm of the PVC pipe was left protruding above the surface of the peat soil and the open end of the pipe was covered to protect the sensor and PTFE sleeve from the ingress of debris (Fig. 5).

2.4. The integration of temperature and atmospheric pressure

The GMM220 NDIR Vaisala CARBOCAP sensor used in this study does not measure pressure and temperature and therefore could not automatically compensate for changes in atmospheric pressure and temperature variations. To compensate for these components in the system it was necessary to measure the atmospheric pressure and temperature components on site. Atmospheric pressure was measured using a UNI-T UT330C USB data logger barometric probe which was placed at the pool bank 100 mm above ground level. Water temperature was recorded using a HOBO Pendant temperature data logger (UA-001-08) placed circa 100 mm below the surface of the pool water, a second logger was placed about 100 mm above ground level to record air temperature and a third temperature logger was placed approximately 50 mm

Fig. 6. NDIR module transmitter: component board, cable and a CO₂ probe for field installation (a) pool assembly and (b) peat zone assembly – components labeled 1–12 (1 Land surface, 2 Water surface, 3 Mesh-net, 4 Transmitter, data-logger, switch & timer, 5 Float assembly, 6 Perforated PVC pipe, 7 Coiled cable & power line, 8 NDIR sensor, 9 Inner perforated protective housing, 10 Sealing lid, 11 Sensor fastening cables, 12 Water temperature probe).

below the peat-soil surface to record near-surface ground temperature. These parameters were measured on an hourly basis throughout the study period.

2.5. Theory and calculation

To calibrate the GMM220 NDIR pool and peat-based sensor outputs it was necessary to adjust for the partial pressure of CO₂ (p_{CO_2}) based on the recorded changes in temperature and total atmospheric pressure (Baehr and DeGrandpre, 2004; Dinsmore, 2008). This approach is based on Henry's universal gas law and states that the mass of a gas that dissolves in a defined volume of water is directly proportional to the pressure of the gas as long as the gas does not react with the water: $C_{\text{gas}} = K_h \times P_{\text{gas}}$ (Plummer and Busenberg, 1982). In this equation, C_{gas} is the concentration of the dissolved gas, K_h is Henry's law constant that is temperature dependent (e.g. increases with temperature) and is particular for the specific gas, and the variable P_{gas} which is the partial pressure of the gas above the solution (Plummer and Busenberg, 1982). Based on this law and the instrumental specifications for the Vaisala sensor, CO₂ concentrations were corrected using the following formula: $C_c = C_m - C_T - C_p$ (Tang et al., 2003). In this equation, CO₂ concentrations (C) were expressed in $\mu\text{mol mol}^{-1}$, and the subscripts c , m , T and p designate; corrected, measured, temperature-corrected and pressure-corrected respectively (Tang et al., 2003). The temperature correction was calculated using the formula: $C_T = 14000 (K_T - K_T^2) \left[\frac{25 - T_C}{25} \right]$ (Tang et al., 2003). In this formula, T_C is the temperature ($^{\circ}\text{C}$), $K_T = A_0 + A_1 \times C_m + A_2 \times C_m^2 + A_3 \times C_m^3$, $A_0 = 3 \times 10^{-3}$, $A_1 = 1.2 \times 10^{-5}$, $A_2 = -1.25 \times 10^{-9}$ and $A_3 = 6 \times 10^{-14}$ (Tang et al., 2003). The pressure correction was calculated using the formula: $C_p = K_p \left[\frac{P - 101.3}{101.3} \right]$ (Tang et al., 2003). In this equation, P is the pressure (kPa), $K_p = A \times C_m$ and $A = 1.38$

(Tang et al., 2003). The reference pressure and temperature values for the GMM220 were 101.3 kPa and 25 $^{\circ}\text{C}$. Using the data gathered by the barometric logger and the water and water-soil temperature loggers the appropriate corrections were made to the 'raw' data recorded.

3. Results

3.1. Temperature and atmospheric pressure

This study sought to investigate the winter level of dissolved CO₂ effluxing from a designated pool and peat soil adjacent to it in a blanket peatland in the Wicklow Mountains as knowledge of the carbon dynamics in these ecosystems has a direct bearing on overall atmosphere CO₂ efflux rates and carbon translocation within this landscape type. The investigation took place during the month of December when light levels were at their lowest and photosynthetic activity and respiration levels minimal. Air temperatures during the measurement period were cool but not unusual for this temperate maritime climatic region. The values were consistent with the average reported local air temperature for December of 5.4 $^{\circ}\text{C}$ (Met Eireann, 2017b) and the elevation of the particular location within the Wicklow Mountains. Actual air temperatures during the measurement period ranged from -3°C to 10°C , while water temperature and soil temperature profiles tended to follow the overall pattern of air temperature which is to be expected as these values are substantially driven by air temperature values (Fig. 7). A correlation analysis of the data sets gives a value of 0.427 for air:water temperature and 0.731 for air:soil temperature.

Atmospheric pressure values at the study site were recorded during the same period that the CO₂ values were measured to facilitate adjustment for the effects of partial

Fig. 7. The range in water, soil and air temperatures over the measurement period.

pressure. Total atmospheric pressure values at the site for the period concerned ranged from 943 to 973 hPa and showed a largely stable period during the initial phase of the study followed by an irregular drop in pressure and then a rise, which began to fall back again towards the end of the measurement period.

3.2. CO₂ concentrations in the peatland pool

The concentration of dissolved CO₂ in the pool was recorded over a period of three weeks and outputs indicate that the CO₂ concentrations ranged from approximately 710 $\mu\text{mol mol}^{-1}$ to a peak of 1560 $\mu\text{mol mol}^{-1}$ (Fig. 8). The

Fig. 8. Corrected CO₂ concentrations (pool condition) $\mu\text{mol mol}^{-1}$.

average dissolved CO_2 concentration for the pool was $1046 \mu\text{mol mol}^{-1}$. Water is the solvent in which the CO_2 dissolves and is also the medium through which temperature values affect the ability of CO_2 to dissolve – consequently the temperature of water is the most significant thermal component in modifying the recorded dissolved CO_2 values. Temperature is also regarded as a significant control on microbial CO_2 emissions. Consequently, temperature is also shown (Fig. 8) as an indication of the possible influence this abiotic parameter may have on the CO_2 values measured. It is also interesting to note that the correlation coefficient of the water temperature and the reported CO_2 values over the measurement period shows a weak positive coefficient of 0.248.

3.3. CO_2 concentrations in the peatland soil

The peat soil zone studied is a region of the blanket peatland approximately 3 m from the bank of the pool. The dissolved CO_2 values for the waters within the sample well in the blanket peat show much higher levels of dissolved CO_2 than that recorded in the pool ranging from 18,000 to $58,000 \mu\text{mol mol}^{-1}$ (Fig. 9). The dissolved CO_2 values in the peat soil condition were recorded over the same period that the values measured in the pool were recorded. The average value for dissolved CO_2 in the peat soil was $31,834 \mu\text{mol mol}^{-1}$. Water temperature data is shown alongside the CO_2 data for the same reasons as outlined for the pool set-up. The correlation between water temperature data and dissolved CO_2 data showed a weak negative value of -0.35 .

It is to be expected that the two locations selected for investigation in this mountain blanket peatland would generate different values with respect to the level of dissolved CO_2 . However, this study reveals a scale difference between these two settings, which are in relative terms spatially quite closely aligned. The relative

rates of change in CO_2 concentrations over the measurement period were greater in the pool waters when compared with the values recorded for the waters of the peat well (Fig. 10).

It is also significant to note the temperature component which has a significant influence in on the solubility of gas including CO_2 , shows a weak relationship with the actual values recorded. This clearly suggests that the process of CO_2 solubility in the waters of the peatlands and its subsequent efflux and translocation through the catchment is likely to be controlled by a multiplicity of factors acting in concert.

4. Discussion

4.1. Blanket peatland CO_2 concentration profiles

The profile of CO_2 concentrations recorded for the peatland soil zone ($18,000$ – $58,000 \mu\text{mol mol}^{-1}$) was more than an order of magnitude greater than that recorded for the pool (710 – $1560 \mu\text{mol mol}^{-1}$) at the study site (Figs. 8 and 9). High variability has been reported in the literature for these concentrations in similar settings. Hamilton et al. (1994) reported CO_2 concentrations ranging from 2 to 90 times atmospheric for boreal wetland ponds. Whitfield et al. (2010) suggest that such variability is likely to be a function of the morphology of the sample locations coupled with the extent of surface water pools and the surrounding vegetation community. Indeed, there is likely to be a higher level of heterotrophic and autotrophic respiration in the peat body compared with the situation prevailing in the pools. Additionally, water movement in blanket peatlands represents a significant aspect of their overall biogeochemical dynamics (Holden, 2005). Rezanezhad et al. (2016) report on the dual-porosity of peat which distinguishes a “mobile region” through which water, solutes and colloids move relatively easily,

Fig. 9. Corrected CO_2 concentration (peat soil condition) $\mu\text{mol mol}^{-1}$.

Fig. 10. Relative rates of change for the CO_2 concentration between pool and peat waters.

and an “immobile region” with negligible fluid dynamics. It has been suggested that while advection through the open and connected pores, and matrix diffusion into and within closed pores are the dominant mechanisms controlling solute transport in peat, that only a relatively small number of studies have investigated the effects of the dual-porosity structure of peat on solute transport (Rezanezhad et al., 2016). Thus it is difficult to quantify this component in the reported CO_2 values. However, in order to accommodate for this dynamic and to minimise its potential influence on measured CO_2 values the selected study site was located on a mountain interfluvium such that gravitational fluid inflow was minimal.

The water in blanket peatlands is typically in contact with, and thus influenced by the underlying mineral soil with the potential for associated inorganic and organic carbon (CO_2) enrichment which may add to the values reported in the peat soil zone. However, there is also considerable uncertainty over the local hydrodynamics within blanket peatlands and thus the potential contribution to carbon stocks from allochthonous sources (Holden and Burt, 2003). Noticeable about the pool CO_2 concentrations is that they show relatively rapid short-term fluctuations when compared to the CO_2 profile for the peat soil zone, which presents a much smoother profile (Figs. 8–10). Thus, this data suggests that the peat soil zone may have a much higher level of relative CO_2 inertia and is less susceptible to short term rapid fluctuations. The significance of peat soil saturation and vegetation is well recognised in controlling the heterogeneous distribution of microbial habitats and activity (Rezanezhad et al., 2016). The peat soil CO_2 flux observed has been measured in the water table below the surface vegetation yet this surface

vegetation is relevant as it determines the nature of the detrital feedstock that accumulates as dead organic matter and forms the substrate for microbial activity. The peat soil zone in this study was situated at the transition between lawn and hummock communities and hence the underlying peat soil comprises a higher proportion of vascular plant detrital material, particularly close to the surface. The consequence of this is that underlying peat mass would have a higher fibrous content and an associated higher porosity value. This elevated near surface porosity has a direct bearing on local hydrodynamics and O_2 supply at the microsite and is likely to be an important determinant in the elevated CO_2 values recorded. This coupled with the potential advection of CO_2 , proximity of the water table-atmospheric boundary and relative thermal isolation of the microsite provide a context in which the elevated CO_2 values recorded can be interpreted.

4.2. Temperature response

This study took place during the mid-winter season and accordingly temperatures were most likely to be close to their lowest values and the light levels were at their lowest values given that the study took place over the winter solstice. The temperature profiles for the air, water and soil components at the study site were recorded (Fig. 7). The driving thermal parameter is the air temperature (incident radiation being minimal) and accordingly it would be expected that the water and soil temperatures would follow the air temperature which ranged from -3°C to 10°C over the study period. From an analysis of the data in Fig. 7 it is evident that the water temperature exhibited only moderate to weak correlation with the air temperature with a

coefficient of 0.427. This is somewhat expected given the length of the study or time frame involved and the fact that water has a higher specific heat capacity than air which produces a thermal lag with respect to changing air temperatures. This is not surprising given the mechanistic structure and physical relationships of air, water and soil in the blanket peatland system. It also reflects the multiplicity of other parameters within the system that influence water temperature including, solar radiation, relative humidity, wind speed, water depth, groundwater/matrix water inflow, and the thermal conductivity of the peat matrix material.

It has been well recognised that temperature is an important factor governing decomposition and that there is a general correlation between temperature values and CO₂ generation in soil organic matter (Jauhainen et al., 2014). In this respect respiration Q₁₀ values of circa 2 have been reported for peatlands (Johansson, 2010). Hence it is appropriate to examine the measured data for temperature and CO₂ concentrations at the study site. As noted earlier, although air temperature is the principle source of thermal input to the peatland ecosystem, it is the mechanism by which this thermal energy is conveyed to the CO₂ controlling processes that is important in controlling system outputs. Since water permeates the system and is the medium for CO₂ transport and diffusion it is appropriate that the thermal character of this component is examined. Thus, the water temperature and CO₂ concentrations for the pool and the peat soil zone were compared over the study period (Figs. 8 and 9). Comparing the data arrays from the pool set-up (Fig. 8) results in a weak positive correlation coefficient of 0.248. However, when water temperature and CO₂ values for the peat soil zone are evaluated the resultant correlation value is a weak negative value of −0.35. It has already been recognised that CO₂ and temperature do have a mechanistic association (Johansson, 2010). Thus, it is interesting to note the lack of correlation in the data sets. This suggests that more complex processes are at work in this ecosystem. Indeed, it has been suggested that unravelling the CO₂ thermal feedback effect in blanket peatland ecosystems is particularly difficult, because the diverse range of organic compounds exhibit a wide range of kinetic properties, which determine the intrinsic thermal dynamics of their decomposition. Moreover, several environmental constraints obscure the intrinsic thermal dimensions of substrate decomposition which masks the actual controlling processes within the system (Davidson and Janssens, 2006). Beer et al. (2008) note that fermenting and methanogenic populations decompose the organic matter in a stepwise manner under a successive diminution of free energy. Methanogenic organisms utilise the products of fermentation or reduce CO₂ with hydrogen (H₂) to form CH₄ and CO₂. The accumulation of CO₂ and CH₄ decreases the availability of free energy available to methanogens below threshold values of −25 to −20 kJ mol^{−1} required for ongoing microbial substrate degradation (Beer et al., 2008). Hence further analysis of the CO₂ flux dynamics needs to examine the dominance and dynamics of intermediate chemical species, and the stratified nature of pH variation, nutrient availability and the accumulation

of toxins that limit respiration. Therefore, it will be necessary to examine other parameters of the system in order to develop a more insightful mechanistic understanding of the factors controlling CO₂ concentrations. It is also worth noting that some of the CO₂ response with respect to temperature may not reveal itself as the temperature range is simply too small. Added to this is the fact that the average temperature value is quite low averaging 4.4 °C and that this diminishes the thermal element in controlling the CO₂ concentrations experienced. It may well be that at higher temperatures the correlation could be stronger. Nonetheless the results of this study suggest that other factors in the ecosystem are probably more dominant in controlling the values of CO₂ in the peatland ecosystem or that the thermal component in the system is significantly affected by other biotic and even abiotic elements (Limpens et al., 2008) and underscores the need to view these systems as complex adaptive systems (Levin, 1998).

4.3. Further research

The carbon cycle of blanket peatlands is dependent on a complex of abiotic and biotic parameters and variables interacting in a multiplicity of different ways which consequently presents a significant challenge to the development of system understanding. There have been many attempts to develop system descriptions that address the challenge of this complexity. However, there are also many contrary views on the true significance of different functional processes and the reliability that can be attached to parameter values in these approaches (Tang et al., 2003; Parry et al., 2012).

This study suggests a role for a direct in situ continuous measurement strategy using non-dispersive infrared (NDIR) sensors in combination with a site architecture to evaluate CO₂ concentrations and efflux in water. Such sensors have been applied to this task before (Johnson et al., 2010) but what has been developed here is a field design that allows their use in soil–pore water and pond water analysis in blanket peatlands over extended periods of time. This design provides enhanced reliability in that the sensor maintains a constant position in the fluctuating water table. However, there remains a measure of uncertainty attached to the source of CO₂ as the flux measures may include diffusion from deeper layers and the current approach provides limited vertical temperature profile. Addressing this will require closer examination of peat stratification, temperature variation with depth and CO₂ source dynamics within the site and should form the basis for a more sophisticated expansion of this approach. Understanding the temporal and spatial pattern of system parameters is crucial to a more accurate assessment of the true CO₂ dynamics of these important ecosystems. Additionally, the importance of understanding winter-time fluxes of CO₂ in the northern hemisphere has been well acknowledged (Aurela et al., 2002; Roehm and Roulet, 2003) yet data on these dynamics is fragmented. This work provides a methodological template that facilitates the development of new initiatives to address questions on the relationship of environmental parameters with the scale

and magnitude of temporal and spatial variability of CO₂ in highland and remote blanket peatlands.

4.4. Conclusion

This study sought to investigate the soil pore water and pool water temporal variability of CO₂ concentrations in an Irish mountain blanket peatland and to explore the hydrological pathways that promote storage, transport and efflux of carbon. This was addressed through the development of a novel implementation system for in situ longitudinal monitoring of CO₂ concentrations in a pool and nearby peat soil zone. Given that the study occurred in the mid-winter period it was expected that photosynthetic CO₂ contributions would be minimal and that most of the CO₂ measured was from older sources. The CO₂ concentrations recorded showed significant differences between the pool waters and the peat soil zone. It was interesting to note that the relatively weak relationship between temperature and CO₂ values. Indeed, this is consistent with some other findings which report weak links between soil CO₂ efflux and temperature (Tang et al., 2003). This suggests that other processes have an important role to play in generating the values recorded including plant physiological and phenological factors, and that it would be unwise to draw too strong an interpretation from the measured data regarding the relationship between water temperature and the CO₂ values. The lack of correlation also suggests that the blanket peatland ecosystem behaves as a complex system, where key uncertainties remain regarding the existence of perturbation thresholds, the relative strengths of CO₂ feedback, the role of hydrodynamics, ecosystem structure and function, and trace gas biogeochemistry. A novel dimension that emerges from this study is the distinction between total ecosystem respiration and soil microbial respiration. Since this study occurred in the deep mid-winter period and the peat soil CO₂ effluxes were measured just below the surface of the water table, these resulting CO₂ effluxes are more closely aligned with the soil microbial activity. This is a significant issue in peatland biogeochemistry and underscores the important role of peat water table CO₂ efflux measurements in winter (Zhang et al., 2005). As such these results provide an important input to the spatial disaggregation of the CO₂ budget across ponds and peat soils within a blanket peatland in winter. However, building a deeper understanding of the carbon dynamics within this ecosystem will require further analysis of the system components, the nature of their interaction through the mediation of powerful and frequently also complex causal networks, and the recognition of the associated emergent properties. This is a prerequisite to a more holistic and deeper ecological appreciation of the role of these significant ecosystems within the biosphere.

Conflict of interest

None declared.

Ethical statement

Authors state that the research was conducted according to ethical standards.

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