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Daytime-only measurements underestimate CH₄ emissions from a restored bog

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ABSTRACT

Accurate estimates of methane (CH₄) fluxes from restored peatlands are needed to inform emission factor estimations and reporting. Flux measurements are usually taken during the daytime but such measurements may provide biased estimates of overall CH₄ emissions if night-time fluxes differ from daytime fluxes. Diurnal variations in CH₄ fluxes have been reported for a range of peatland types, but not for restored raised bogs which are important carbon stores in some countries. To help fill this knowledge gap, we investigated diurnal variations in CH₄ emissions from a restored raised bog. CH₄ fluxes from a restored raised bog were measured in two 24-hr field campaigns using flux chambers. Carbon dioxide (CO₂) fluxes were also monitored, as were a suite of complementary environmental variables. Night-time CH₄ fluxes were significantly greater than daytime fluxes during both campaigns, by 10.4% and 36.1%, respectively. In Campaign 1 air temperature was the best predictor of CH₄ fluxes, whereas in Campaign 2 net ecosystem exchange (NEE) values were the best predictor. This study shows that diurnal variations in CH₄ fluxes exist in a restored peatland and that current approaches biased to daytime measurements will underestimate CH₄ emissions from restored peatlands to the atmosphere.

RÉSUMÉ

Des estimations précises des flux de méthane (CH₄) à partir de tourbières perturbées sont requises pour informer les estimations de facteurs d'émission et la production de rapports. Les mesures de flux sont généralement prises pendant le jour, mais de telles mesures peuvent fournir des estimations biaisées des émissions totales de CH₄ si les flux nocturnes diffèrent des flux diurnes. Les variations journalières des flux de CH₄ de différents types de tourbières ont déjà été rapportés, mais pas pour les tourbières ombrotrophes restaurées, qui sont d'importants réservoirs de carbone dans certains pays. Pour combler ce manque de connaissances, nous avons évalué les variations journalières des émissions de CH₄ d'une tourbière ombrotrophe restaurée. Les flux de CH₄ ont été mesurés lors de deux campagnes de terrain de 24 heures à l'aide de chambres de débit. Les flux de dioxyde de carbone (CO₂) ont aussi été enregistrés, tout comme une série de variables environnementales complémentaires. Les flux de CH₄ nocturnes étaient significativement plus élevés que les flux diurnes lors des deux campagnes, respectivement par 10,4% et 36,1%. Lors de la Campagne 1, la température de l'air était le meilleur prédicteur des flux de CH₄, tandis que lors de la Campagne 2, les valeurs d'échanges écosystémiques nets (EEN) étaient le meilleur prédicteur. Cette étude montre que des variations journalières des flux de CH₄ sont présentes dans une tourbière ombrotrophe restaurée et que les approches actuelles basées sur les mesures diurnes sous-estiment les émissions de CH₄ vers l'atmosphère.

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Introduction

Peatlands that have been previously drained, but are now rewetted can be significant sources of atmospheric CH₄ (Lai 2009). The United Nations Framework Convention on Climate Change and the Kyoto Protocol require signatories to report greenhouse gas (GHG) emissions annually. However, guidance from the Intergovernmental Panel on Climate Change (IPCC) on emissions factors specific to CH₄ fluxes from rewetted organic soils is only recent (IPCC 2014). Rewetted peatlands are in the category of

Agriculture, Forestry and Other Land Use, and this category produced 24% of the global anthropogenic GHG emissions between 2000 and 2009 (IPCC 2013; Wilson et al. 2015). The Tier 1 default CH₄ emission factor for temperate nutrient-poor rewetted organic soils, based on data from 42 studies, is 33.6 mg CH₄ m⁻² day⁻¹, with a large variance of 1.1–162.5 mg CH₄ m⁻² day⁻¹ (IPCC 2014). To help reduce the uncertainty in this estimate, countries are advised to develop more locally representative emissions factors so that differences between study sites, such as time since

rewetting, vegetation composition, prior land use, and drivers of CH₄ fluxes can be taken into account (IPCC 2014; Wilson et al. 2016).

To improve estimates of emissions factors, it is important that measurements of CH₄ fluxes from restored peatlands are made and are as accurate as possible. Methane fluxes from peatlands are typically measured using flux chambers. Automatic and manually-operated chambers may be used (Denmead 2008), but, due to their lower cost, manual chambers are more commonly deployed. Manual flux chamber measurements are usually made in the daytime, and it is often assumed that the daytime flux is representative of night-time fluxes. This assumption is then carried forward into estimation of seasonal or annual fluxes, and subsequently calculations of emissions factors (Dise et al. 1993; Van Den Pol-Van Dassel et al. 1999; Bubier et al. 2005; Davidson and Janssens 2006; Pelletier et al. 2007).

A number of studies have looked at diurnal fluctuations in CH₄ fluxes from peatlands (Whalen and Reeburgh 1988; Yavitt et al. 1990; Mikkilä et al. 1995; Shannon et al. 1996; Hargreaves and Fowler 1998; Greenup et al. 2000; Bäckstrand et al. 2008; Lai et al. 2012; Kowalska et al. 2013), and some show that large variations between day and night can occur (approx. 20% [Bäckstrand et al. 2008], 33% [Hargreaves and Fowler 1998], 41.1–74.6% [Lai et al. 2012]). However, little or no work has been done on restored peatlands, particularly restored raised bogs. Raised bogs are ombrotrophic, and are characterised by the formation of a dome of peat, usually rising from a level, lowland topography (Lindsay 2010). Raised bogs have been widely drained for agriculture, forestry and peat harvesting, and are now the target of extensive restoration efforts (Campeau and Rochefort 1996; Pfenhauer and Klötzli 1996; Komulainen et al. 1999; Francez et al. 2000; Tuittila et al. 2004; Wilson et al. 2007; Howie et al. 2009; Herbst et al. 2013; Andersen et al. 2017). In the UK approximately 20 km² of raised bogs have been subject to restoration management (Baird et al. 2009; Worrall et al. 2011). To help improve understanding of CH₄ emissions from restored raised bogs, we undertook two 24-hour campaigns of measurements at a site in the east of England. In each campaign, we measured CH₄ fluxes, and also CO₂ fluxes and a range of environmental parameters to see if they can explain any CH₄ flux variations.

Materials and methods

Study site

Our investigation took place at Thorne Moors, a lowland raised bog in South Yorkshire, UK (53°4'N, 0°5'W). A

large area of Thorne Moors had been previously drained and the peat extracted using milling machinery. Restoration work started in the late 1990s through drain blocking and the creation of bunded compartments to help raise water tables. Many areas are now dominated by cotton-grasses (*Eriophorum* spp.), as are other peatlands with a similar history (Komulainen et al. 1998; Tuittila et al. 2000b; Marinier et al. 2004; Lavoie et al. 2005). The area in which measurements were taken has been under restoration management since 1997 when drains were blocked and has a vegetation cover dominated by both *Eriophorum angustifolium* Honck. and *Eriophorum vaginatum* L.

Overall study design

To investigate diurnal variations in CH₄ emissions, two 24-hr campaigns of gas flux measurements were carried out, one in July 2012 (Campaign 1) and one in July 2015 (Campaign 2). In Campaign 1 conditions were overcast and there was little diurnal variation in air temperatures. In contrast, clear skies predominated in Campaign 2, with air temperature differing substantially between day and night (see below). *E. angustifolium* and *E. vaginatum* were equally abundant in the study area, and monitoring locations reflected this (Table 1).

In both campaigns CH₄ and CO₂ fluxes were measured using manual flux chambers. Chamber design differed between the campaigns. In Campaign 1 four static chambers were deployed (Denmead 2008) and tests on these were started every 90 minutes and lasted for 20 minutes. Samples of gas were collected using syringes, with five samples collected per test over the 20 minutes. These samples were later analysed in the laboratory (see below). During Campaign 2 six chambers were used, and fluxes were again measured every 90 minutes. However, this campaign used a portable gas analyser (Los Gatos Research Ultra-portable Greenhouse Gas Analyser, California, USA) and represented a dynamic chamber setup (see Denmead 2008). This equipment measured gaseous concentrations instantaneously at one second intervals, allowing test times at each chamber to be reduced to three minutes. Both campaigns yielded 16 sets of measurements, giving 160 tests in total.

Collar and flux chamber design

Collar and chamber designs for Campaign 1 followed those of Stamp (2011). Collars were constructed from 0.004 m thick sheets of polyvinyl chloride (PVC), and covered an area of 0.105 m². Chambers were constructed from clear acrylic, which was transparent to photosynthetically active radiation (PAR) and had a

Table 1. Collar identification system.

Collar ID	Campaign number	Collar number	Main plant cover (% coverage)	Other vegetation (% coverage)
C1_1EV	1	1	<i>E. vaginatum</i> (90%)	<i>E. angustifolium</i> (approx. 25%)
C1_2EV	1	2	<i>E. vaginatum</i> (80%)	<i>E. angustifolium</i> (approx. 25%)
C1_3EA	1	3	<i>E. angustifolium</i> (100%)	None
C1_4EA	1	4	<i>E. angustifolium</i> (95%)	<i>Sphagnum cuspidatum</i> (< 10%)
C2_1EA	2	1	<i>E. angustifolium</i> (100%)	None
C2_2EV	2	2	<i>E. vaginatum</i> (85%)	<i>E. angustifolium</i> (<20%)
C2_3EV	2	3	<i>E. vaginatum</i> (90%)	<i>E. angustifolium</i> (<10%)
C2_4EV	2	4	<i>E. vaginatum</i> (75%)	<i>E. angustifolium</i> (<30%)
C2_5EM	2	5	Equal mix <i>E. angustifolium</i> and <i>E. vaginatum</i> (100%)	None
C2_6EA	2	6	<i>E. angustifolium</i> (100%)	None

volume of 0.032 m³. During chamber tests, a gas-tight seal between the collar and chamber was achieved by filling with water a gutter fitted to the top of the collar. A Commeter C4141 thermo-hygro-barometer (Comet Systems, Czech Republic, temperature precision 0.1°C and accuracy ±0.4°C, pressure precision 0.1 hPa and accuracy ±2 hPa) was fitted into the chambers to give air temperature and barometric pressure readings during tests. A small handheld fan was fitted inside the chamber to mix the air, and an uninflated balloon was fitted over an open tube fixed through the chamber lid to allow for pressure equilibration. A septum was fitted into the lid of the chambers for the removal of gas samples via syringe. After collection, gas samples were injected into 12 mL pre-evacuated vials (Labco, Lampeter, UK) to be transported back to the laboratory. Gas samples were analysed for their CH₄ and CO₂ content using an Agilent 7890A gas chromatograph fitted with a flame ionisation detector (Agilent Technologies, Cheshire, UK).

Larger collars (0.36 m²) and chambers (0.25 m³) were used for Campaign 2, each made from the same materials as per Campaign 1. The inlet and outlet tubes from the portable gas analyser were fitted into the chamber through a bung in the chamber wall. An axial fan was fitted inside the chamber to mix the air. Pressure equilibration was achieved through two partially inflated gas bags, one inside and one outside the chamber, connected via a tube fixed through the chamber wall. As per Campaign 1, a Commeter C4141 thermo-hygro-barometer was used for monitoring chamber pressure and air temperature. In both campaigns the chambers were left unshrouded to measure net ecosystem CO₂ exchange (NEE).

Flux calculations

Flux calculations

Fluxes were calculated by applying linear regression to the CH₄ vs time and CO₂ vs time data for each chamber test (Denmead 2008). The regression fit was only

accepted if $r^2 > 0.8$ and $p < 0.05$. Fluxes for data sets that did not meet these criteria were rejected with one exception: if the variation in gas concentrations during a test were within a threshold error range, the flux was assumed to be zero (0.03 ppm for CH₄ and 3 ppm for CO₂). Individual chamber fluxes were calculated as mg m⁻² day⁻¹, where positive values indicate net release to the atmosphere and negative values indicate net uptake from the atmosphere. To compare these individual fluxes to a sum of all the fluxes measured in a 24-hr period per collar per gas, each individual flux was converted from mg m⁻² day⁻¹ to mg m⁻² 90 minutes⁻¹ (the duration between one test and the next on the same collar). For each collar and each gas, the 16 flux results (mg m⁻² 90 minutes⁻¹) could then be summed to give a flux over the 24 hours (mg m⁻² day⁻¹). Any flux that is a summed total over the 24 hours will be termed a total flux. CO₂ fluxes are presented as net CO₂ fluxes (NEE).

Radiative forcing

The radiative forcing effect of a peatland in terms of its net GHG emissions can be calculated in terms of carbon dioxide equivalents (CO₂-e). The CH₄ fluxes were converted into CO₂-e by multiplying by 28, the current IPCC estimate for the global warming potential (GWP) of CH₄ on a 100-year timescale (IPCC 2013). The resulting figure was then added to the total NEE to give a total CO₂-e per collar. To gauge the effect of daytime-only CH₄ flux estimates on the overall CO₂-e budget, we repeated the calculations above, but used a total CH₄ flux based on daytime-only measurements (total daytime CH₄ flux).

Environmental and meteorological variables

Environmental and meteorological variables were measured alongside gaseous fluxes to be used as candidate explanatory variables for flux variations. During both campaigns an automatic weather station (AWS – Vantage Pro2, Davis Instruments, USA), located 60 m from the sampling area, was used to record hourly

averages of air temperature and barometric pressure, and hourly rainfall totals. In Campaign 1 between 21:00 and 11:00 there was a partial power malfunction with the AWS. Barometric pressure and rainfall were still logged; however, air temperature data was not recorded. A nearby farm (approx. 3 km away) had an AWS of the same specifications, so it was possible to use the air temperature data from this AWS to model the air temperatures between 21:00 and 11:00 at our study site. During Campaign 2 a second temperature sensor (Diver DI 501, Van Walt Ltd., Surrey, UK, accuracy: $\pm 0.1^\circ\text{C}$, precision: 0.01°C) was located at the AWS and used to record air temperature at one-minute intervals.

In Campaign 1 manual measurements of soil temperature at 10 cm depth (Grant, UK, accuracy: $\pm 1.5\%$, precision: 0.1°C) and readings of PAR (PAR Quantum sensor, Skye Instruments, UK, error: max. 5%) were taken adjacent to one collar every 90 mins (PAR readings were not taken during the night). For all collars, water-table depth (WTD) was measured manually from a dipwell (polypropylene, 32 mm diameter, 50 cm length with four columns of 8 mm holes at 10 cm intervals, each column offset by 5 cm) adjacent to the collar. As with temperature and PAR, WTD readings were taken every 90 minutes (i.e., during every chamber flux test). During Campaign 2 soil temperature at 15 cm depth was logged at 15-minute intervals adjacent to each collar (TinyTag TGP-4520, Gemini Data Loggers, Chichester, UK, accuracy: $\pm 0.35^\circ\text{C}$, precision: 0.02°C). WTD was logged every 15 minutes from a dipwell installed adjacent to each collar using a pressure transducer (Diver DI 501, Van Walt Ltd., Surrey, UK, accuracy: ± 0.5 cm water level, precision: 0.2 cm). PAR was measured during each daytime chamber flux test.

Statistical analysis

To test whether there were diurnal variations in CH_4 emissions, daytime and night-time fluxes were compared using paired *t*-tests in Microsoft Excel 2013. The mean flux for each collar during each day or night period was calculated, and a paired *t*-test applied to these mean flux values for each campaign (Campaign 1, $n = 4$ tests, Campaign 2, $n = 6$). Differences were considered to be significant where $p < 0.05$. Multiple stepwise linear regression (IBM SPSS Statistics 21) was used for each gas individually on a per-collar basis to determine the environmental controls on the CH_4 fluxes, and thus address the secondary aim of this study. The independent variables considered in each regression model were: soil temperature, air temperature, barometric pressure, WTD and NEE for the collar in question.

Results

Environmental and meteorological variables

The barometric pressure ranged from 1018.6 hPa at 14:00–17:00 to 1021.8 at 01:00 during Campaign 1 and from 1017.1 hPa at 13:00 to 1021.1 hPa at 01:00 during Campaign 2. Figure 1a shows that during both campaigns there was very little variation in WTD over 24 hours. The water table was closer to the peat surface in Campaign 1, whereas in Campaign 2 the water table was more spatially varied. Figure 1b shows the soil temperatures during both campaigns. In Campaign 1 the soil temperatures were more varied at the start of the campaign than at the end. During Campaign 2 diurnal variation in soil temperature is evident, with a rise in soil temperature at 15 cm depth during the evening and early night hours, consistent between all six collars. Figure 1c shows the PAR and air temperatures for both campaigns, where the difference in diurnal variation between the two campaigns is most apparent. Both variables had a much larger diurnal range in Campaign 2 than in Campaign 1. There was almost constant cloud cover during Campaign 1, compared with very few clouds during Campaign 2. Campaign 1 had a diurnal air temperature range of 7.5°C , compared with 21.6°C in Campaign 2. PAR levels reached a peak of $620 \mu\text{mol m}^{-2} \text{s}^{-1}$ in Campaign 1, compared with $1573 \mu\text{mol m}^{-2} \text{s}^{-1}$ in Campaign 2.

Methane fluxes

Overall, CH_4 fluxes were greater during Campaign 1 than Campaign 2 (Figure 2a). Table 2 shows that only two chamber tests in Campaign 1 and one chamber test in Campaign 2 did not meet the flux calculation criteria. In both campaigns, night-time CH_4 fluxes were significantly greater than daytime fluxes ($p < 0.001$ for Campaign 1, $p = 0.001$ for Campaign 2). The night-time peaks of CH_4 flux were at similar times: 02:00 during Campaign 1 ($94.9 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) and 02:30 during Campaign 2 ($67.8 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$). On average, CH_4 fluxes were 10.4% and 36.1% higher at night than during the day in Campaigns 1 and 2 respectively. Table 2 also shows the percentage difference in the CH_4 flux between night and day for individual collars.

Carbon dioxide exchanges

Net ecosystem CO_2 exchanges (NEE) were used as a candidate independent variable in the regression

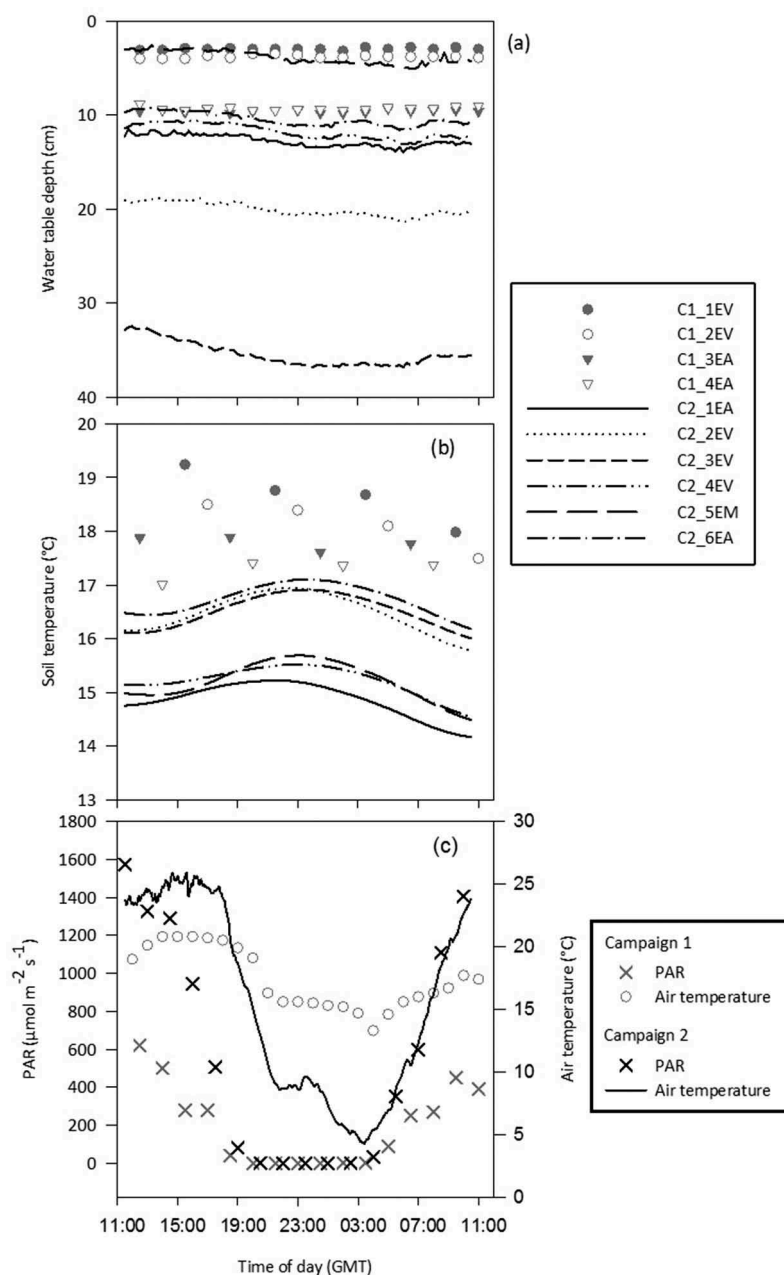


Figure 1. Environmental and meteorological variables measured during both campaigns: (a) WTD (note the inverted y-axis: 0 = peat surface); (b) soil temperature; and (c) PAR and air temperature.

models (see below) and were also used in the estimation of $\text{CO}_2\text{-e}$. Figure 2b shows that there was the expected diurnal pattern in NEE during both campaigns, with night-time losses of CO_2 and net daytime uptakes or lower rates of loss. Over the 24-hr period there was a net CO_2 loss from each collar in Campaign 1 (Table 2). In comparison, Campaign 2 had a higher rates of CO_2 uptake during the day and a net CO_2 uptake in each collar. Table 2 also shows that not all CO_2 chamber tests met the flux

calculation criteria, including none at the 06:30 test during Campaign 1.

Radiative forcing

Table 2 shows the total CH_4 fluxes and NEE values for both campaigns, and also the total $\text{CO}_2\text{-e}$. During Campaign 1, the total NEE was positive from every collar (release to the atmosphere). During Campaign 2, the total NEE from each collar was negative, and

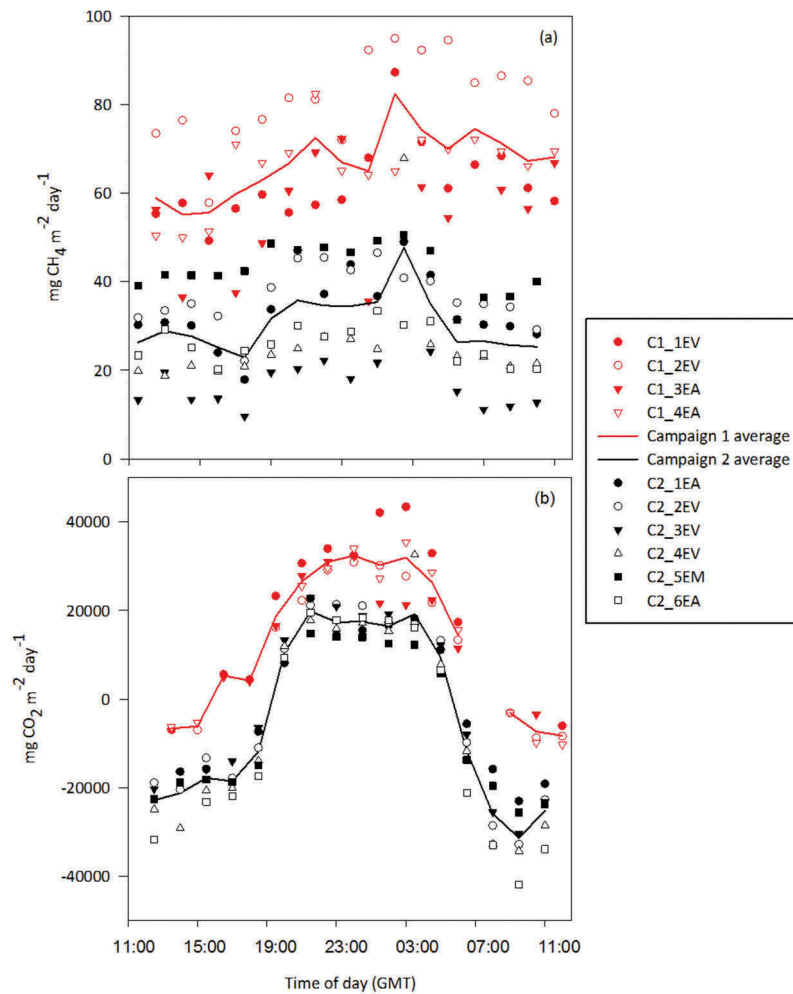


Figure 2. Gaseous fluxes from both campaigns of: (a) CH₄; and (b) NEE. In Campaign 1 at 06:30 none of the four chamber tests resulted in an acceptable NEE estimate; hence, the data gap.

because the CO₂-e values from the CH₄ fluxes were smaller than in Campaign 1, the overall radiative forcing was still negative for each collar. Table 2 also shows the bias in CO₂-e that can be introduced when differences between daytime and night-time CH₄ fluxes are not accounted for. Values for total CO₂-e were calculated using total CH₄ flux and using only total daytime CH₄ flux values. Only using total daytime CH₄ flux values led to an underestimation in CO₂-e compared to when both daytime and night-time CH₄ fluxes were accounted for. The average underestimation in CO₂-e was 5.4% (range: 4.0–7.2%) in Campaign 1, and 12.4% (range: 3.9–31.4%) in Campaign 2.

Environmental controls on CH₄ fluxes

Table 3 shows the results of the stepwise multiple regressions. Air temperature was a significant explanatory variable in three out of four collars during Campaign 1, with colder night-time air temperatures

associated with larger CH₄ emissions. For collar C1_3EA (see Table 1 for collar codes) no significant relationships were found. In collar C1_2EV WTD was a significant variable alongside air temperature. For Campaign 2 NEE was a significant variable in all six collars, with larger CO₂ emissions associated with larger CH₄ emissions. Soil temperature was an additional significant variable in collar C2_1EA, as was WTD in collar C2_5EM.

Discussion

Diurnal CH₄ flux variation

This study has shown that CH₄ fluxes from a restored lowland raised bog dominated by *Eriophorum* spp. are significantly larger during the night than the day. Of previous studies into diurnal CH₄ fluxes where *Eriophorum* spp. were an important component of the vegetation, some found that daytime CH₄ fluxes exceed

Table 2. Average and total fluxes of CH₄, NEE, and CO₂-e for each campaign.

Collar	Daytime average CH ₄ flux (mg m ⁻² day ⁻¹) ±SE (n)	Night-time average CH ₄ flux (mg m ⁻² day ⁻¹) ±SE (n)	% difference between night-time and daytime CH ₄ fluxes	Total CH ₄ flux (mg m ⁻² day ⁻¹) (n)	Total CH ₄ flux as CO ₂ -e (mg m ⁻² day ⁻¹)	Total NEE (mg CO ₂ m ⁻² day ⁻¹) (n)	Total CO ₂ -e (mg m ⁻² day ⁻¹)	Total CO ₂ -e if only total daytime CH ₄ flux used	Underestimation of total CO ₂ -e (mg m ⁻² day ⁻¹) if only total daytime CH ₄ flux used (%)
C1_1EV	59.4 ± 1.7 (10)	66.4 ± 4.9 (6)	11.8	62 (16)	1736	15,805 (12)	17,541	16,844	697.2 (4.0)
C1_2EV	78.8 ± 3.1 (10)	85.7 ± 3.6 (6)	8.8	81.3 (16)	2276.4	10,252 (12)	12,528	11,630	897.5 (7.2)
C1_3EA	53.5 ± 3.6 (9)	59.8 ± 6.4 (5)	11.8	48.8 (14)	1366.4	11,863 (12)	13,229	12,705	524.0 (4.0)
C1_4EA	63.7 ± 2.9 (10)	69.6 ± 2.8 (6)	9.3	65.9 (16)	1845.2	10,053 (13)	11,898	11,167	731.4 (6.2)
C2_1EA	29.8 ± 1.8 (11)	42.8 ± 2.5 (5)	43.5	33.9 (16)	947.9	-2140.3 (16)	-1192.4	-1566.5	374.1 (31.4)
C2_2EV	33.4 ± 1.5 (11)	44.1 ± 1.1 (5)	32.2	36.7 (16)	1028.4	-3348.6 (16)	-2320.3	-2706.3	386.0 (16.6)
C2_3EV	14.9 ± 1.3 (11)	20.6 ± 0.9 (4)	38.1	15.4 (15)	430.7	-2307.3 (14)	-1876.6	-2020.5	144.0 (7.7)
C2_4EV	21.6 ± 0.6 (11)	34.4 ± 8.4 (5)	59.1	25.6 (16)	717.2	-6136.8 (16)	-5419.7	-5720.6	300.9 (5.6)
C2_5EM	40.5 ± 1.5 (11)	48.3 ± 0.7 (5)	19.1	43 (16)	1202.7	-5899.9 (16)	-4697.2	-5119.5	422.3 (9.0)
C2_6EA	24.1 ± 1.1 (11)	30 ± 1.0 (5)	24.3	26 (16)	726.5	-7451.5 (15)	-6725	-6987.2	262.2 (3.9)

Positive flux values indicate release to the atmosphere, negative values uptake. Positive % indicates that night-time fluxes > daytime fluxes. Number in brackets represents number of samples over time, with the exception of the final column where they represent a %.

night-time fluxes (Yavitt et al. 1990; Fan et al. 1992; Thomas et al. 1996; Waddington et al. 1996; Bäckstrand et al. 2008), with fewer finding that night-time fluxes exceeded those during the day (in agreement with this study) (Yavitt et al. 1990; Shannon et al. 1996; Waddington et al. 1996; Lai et al. 2012), and in some cases no patterns or differences between day and night were found (Whalen and Reeburgh 1988; Mikkilä et al. 1995; Greenup et al. 2000; Bäckstrand et al. 2008). Other studies on different vegetation types or different peatland types report results that differ from what we found here (Waddington et al. 1996; Bäckstrand et al. 2008). The majority of the diurnal studies cited above conducted fieldwork in summer months (June–August). Yavitt et al. (1990) found different results between summer and autumn field studies. In June and August, night-time CH₄ fluxes were greater than daytime fluxes, but in October daytime CH₄ fluxes were greater than night-time fluxes (Yavitt et al. 1990). Differences between daytime and night-time fluxes might not be consistent throughout the year, and so the effect of diurnal variations on yearly estimates of CH₄ emissions remains somewhat uncertain. Across all of the cited studies above, only two studies were found that had clearly used statistical analysis (*p*-values stated) to examine whether there were significant diurnal variations in CH₄ fluxes from peat bogs (Mikkilä et al. 1995; Bäckstrand et al. 2008).

To our knowledge, ours is the first study to investigate diurnal variation in CH₄ fluxes on a restored bog. Peatland restoration often involves the reestablishment of vegetation on previously bare peat surfaces. Therefore, a better understanding of how different vegetation types influence diurnal variations in CH₄ flux is imperative to improve our knowledge of the impact of peatland restoration on GHG emissions, and, therefore, emissions factors. Many studies have observed that *Eriophorum* spp., particularly *E. vaginatum*, are commonly the first species to colonise under restoration management (Lavoie and Rochefort 1996; Tuittila et al. 2000b; Lavoie et al. 2003; Marinier et al. 2004; Poulin et al. 2005; Wilson et al. 2009, 2013; Haapalehto et al. 2011; Karofeld et al. 2016). Often the establishment of an *Eriophorum* spp. cover can facilitate the establishment of other species, such as bryophytes (Sliva and Pfadenhauer 1999; Tuittila et al. 2000b; Lavoie et al. 2003). If vegetation cover is one of the most important drivers of diurnal CH₄ flux patterns, then changes in vegetation following peatland restoration (Komulainen et al. 1999; Kozlov et al. 2016) could have an important effect on CH₄ flux estimates, and should be a focus of future research in this area. All of the studies cited above on the presence

Table 3. Stepwise multiple linear regression results on a per-collar basis for drivers of CH₄ fluxes.

Collar	Adjusted r^2 value	WTD		Barometric pressure		Air temperature		Soil temperature		NEE	
		Beta	p -value	beta	p -value	beta	p -value	Beta	p -value	beta	p -value
C1_1EV	0.36	0.33	0.179	-0.17	0.847	-0.65	0.023	-0.29	0.269	0.30	0.473
C1_2EV	0.57	0.61	0.025	-0.54	0.262	-0.91	0.003	-0.12	0.661	-0.18	0.540
C1_3EA	-	-	-	-	-	-	-	-	-	-	-
C1_4EA	0.61	-0.06	0.771	0.06	0.913	-0.80	0.001	0.11	0.584	-0.36	0.222
C2_1EA	0.70	0.19	0.294	0.18	0.314	-0.35	0.158	-0.44	0.049	1.11	<0.001
C2_2EV	0.58	0.18	0.302	0.30	0.074	-0.42	0.067	-0.30	0.495	0.78	<0.001
C2_3EV	0.75	0.10	0.592	0.18	0.238	-0.33	0.088	-0.46	0.300	0.87	<0.001
C2_4EV	0.34	0.11	0.607	0.16	0.477	-0.18	0.590	-0.61	0.081	0.62	0.010
C2_5EM	0.80	-0.41	0.008	-0.04	0.881	0.16	0.653	-0.57	0.094	1.01	<0.001
C2_6EA	0.75	0.01	0.926	0.12	0.383	-0.26	0.202	-0.05	0.908	0.87	<0.001

p -Values marked in bold are significant at $p < 0.05$.

or absence of diurnal CH₄ variations focussed on areas containing multiple vegetation types, and no information on the abundance of different plant species within the gas flux collars was given, unlike in this study (Table 1). It would be useful for future studies to provide detailed information on the abundance of different plant species within gas flux collars, or to focus on areas dominated by one species, to increase our understanding of the potential effects of vegetation on diurnal variations in CH₄ fluxes.

Drivers of CH₄ fluxes

Diurnal variations in CH₄ fluxes may be explained by two sets of processes. Firstly, diurnal cycles of soil temperature will affect the rates of activity of methanogenic or methanotrophic archaea and bacteria, respectively (Dunfield et al. 1993; Le Mer and Roger 2001; Serrano-Silva et al. 2014), which in turn will affect CH₄ fluxes. Secondly, photosynthetic activity during the day, and the resulting production of root exudates, may provide readily decomposable substrates to methanogens, enabling and thus affecting their production of CH₄.

The results from the regression modelling suggest that soil temperature variation at the study site was, with the exception of one collar, insufficient to have an effect on CH₄ fluxes, and thus contrasts with the findings of Mikkela et al. (1995) and Shannon et al. (1996) who found negative relationships between diurnal CH₄ fluxes and soil temperature. Shannon et al. (1996) reported lags of between 1 and 5 hours from the maximum peat temperature at 5 and 10 cm depths to the maximum CH₄ flux, whilst Mikkela et al. (1995) found varying temporal lags in peat temperature (2–10 hours) resulted in significant relationships with CH₄ flux. Measured changes in soil temperature at our study site were modest, and there were no clear diurnal patterns in soil temperature in Campaign 1, while in Campaign 2 soil temperatures varied by only between 1

and 1.3°C. Therefore, it is not surprising that soil temperature did not figure as an explanatory variable in all but one of the collars.

In Campaign 1 air temperature was found to be an important explanatory variable, while in Campaign 2 this was replaced by NEE. In both cases the relationship can be interpreted in terms of plant substrate provision to methanogens and a lag between this provision and CH₄ production and subsequent transfer to the ground surface. The relationship between CH₄ flux and air temperature was negative, meaning that the highest fluxes were when air temperatures were lowest. Photosynthate production will tend to be highest during the day when air temperatures are highest, so this result suggests that there is a lag of approximately half a day between: (1) photosynthate production; and (2) the subsequent production of CH₄ and its transport via diffusion through soil and plant tissue to the atmosphere. The relationship between CH₄ flux and NEE found in Campaign 2 is consistent with this interpretation. There was a direct (positive) relationship between the two variables. Higher rates of photosynthesis and net CO₂ uptake produce a negative NEE, and the direct relationship in the regression means that CH₄ fluxes were highest when NEE was positive (no photosynthesis) and lowest when NEE was most negative, again suggesting that highest CH₄ fluxes occurred about half a day after maximal rates of photosynthate production.

The interpretation above has some support in the literature. Bäckstrand et al. (2008) found the same positive relationship between CH₄ fluxes and NEE, but only for night-time fluxes. Similarly, Greenup et al. (2000) found a significant positive correlation between night-time CH₄ and CO₂ fluxes. Several studies have found links between recently-fixed photosynthates and CH₄ emissions on peatlands dominated by *Eriophorum* spp. (Waddington et al. 1996; Tuittila et al. 2000a; Ström et al. 2003; Marinier et al. 2004; Lai et al. 2014). There is evidence that *Eriophorum* spp. can

quickly transfer recently-fixed photosynthates to root exudates (Ström et al. 2003). Lag times of 2–24 hours have been reported between uptake of labelled C during photosynthesis and emission of that C as CH₄ (King and Reeburgh 2002; King et al. 2002; Ström et al. 2003). King and Reeburgh (2002) and King et al. (2002) found that, although CH₄ derived from these recent photosynthates was emitted within 24 hours, the peak emission rates from the photosynthates came at 5–7 days. Without further work using isotopically-labelled C, it is unclear if the CH₄ fluxes measured in our study were derived from recently-fixed photosynthates (timescale of hours) or from a longer period going back a number of days. Campaign 2 saw greater rates of CO₂ uptake and so more photosynthate fixation than in Campaign 1. If a rapid (<24 hours) transfer of photosynthates to root exudates through to CH₄ production, transport and emissions occurred, higher CH₄ emissions would be expected in Campaign 2; however, as Figure 2b shows, the CH₄ emissions in Campaign 2 were consistently lower than in Campaign 1. The WTD in Campaign 2 were lower than in Campaign 1 (Figure 1a), which may explain why CH₄ emissions in Campaign 2 were lower than in Campaign 1, due to a smaller anoxic zone for methanogenesis and a larger oxic zone for methanotrophy. However, WTD was not found to be a significant variable in this study, except for C2_5EM which had the highest WTD in Campaign 2. Unfortunately, we did not collect solar radiation data prior to both campaigns. In future research, such analyses may provide insight into links between photosynthate fixation and CH₄ fluxes.

Improving CH₄ flux estimation

Improving emissions factors for rewetted peatlands is vital for governments to be able to accurately fulfil their obligations to the Kyoto Protocol. In rewetted peatlands, when daytime and night-time CH₄ fluxes are known to be different, measuring a flux just once during a day will result in an over- or underestimation of the true total CH₄ flux during that particular day. This study highlights the wide range of different results that could be gained from just one daytime measurement on a particular collar, and be taken forward into seasonal and annual estimations, from which emissions factors could then be calculated. In Campaign 1 the variation in daytime CH₄ fluxes from one collar ranged from 19.1 to 36.7 mg m⁻² day⁻¹ (C1_1EV and C1_2EV respectively). In Campaign 2 these variations ranged from 7.1 to 23.6 mg CH₄ m⁻² day⁻¹ (C2_4EV and C2_1EA respectively). These results highlight the

variation that could occur if only one daytime CH₄ flux measurement is taken at each collar. Measuring daytime CH₄ fluxes more than once in a day may lead to an improvement in flux and emission factor estimation. Total CH₄ fluxes and individual recorded fluxes during both campaigns were compared for each collar, yet no optimum time for CH₄ flux measurements could be found. The times when the recorded CH₄ flux was most similar to the total flux varied between collars: C1_1EV and C1_4EA both 09:30, C1_2EV 21:30, C1_3EA 18:30, C2_1EA and C2_6EA both 19:00, C2_2EV and C2_3EV both 05:30, C2_4EV 04:00 and C2_5EM 17:30. Table 2 shows that not accounting for night-time CH₄ fluxes leads to an underestimation in the total CO₂-e flux. If such biases are then carried forward into seasonal and annual flux estimations, this underestimation may be further exacerbated. In most collars across both campaigns this underestimation was <10%, <5% in three of these collars. However, the remaining two collars had larger underestimations of 16.6 and 31.4%. These higher underestimations, and the wide range of underestimations, prevent a blanket approach to address this problem (e.g. a set percentage to increase measured fluxes by on restored peatlands dominated by *Eriophorum* spp.). Both campaigns in this study were conducted in July, and many of the diurnal studies cited earlier in this discussion were also conducted in summer months. Further knowledge on any seasonal variations in diurnal CH₄ flux patterns would be useful; if night-time fluxes at other times of year are smaller than daytime fluxes they may balance out the underestimations found in summer. If night-time CH₄ fluxes are consistently higher than daytime fluxes throughout the year, then the underestimation could be greater than currently thought. Automated chambers may be the best method to conduct diurnal studies in colder months, if available. Increasing the number of flux measurements at one collar may result in a reduction in the number of collars that it is possible to measure during a field visit. Studies at a wider range of field sites should indicate the extent to which a greater spatial or temporal replication of flux measurements would be more beneficial to providing more accurate estimations of CH₄ flux from restored peatlands.

It is common to model CO₂ exchanges using solar radiation and a range of other environmental variables, such as air temperature, as explanatory variables (Tuittila et al. 1999; Samaritani et al. 2011; Görres et al. 2014; Beyer and Höper 2015; Dixon et al. 2015). Although satisfactory models may be found for CO₂ exchanges, similar models may prove more elusive for CH₄. For example, while our results from Campaign 2

might suggest that diurnal variations in CH₄ emissions can be modelled from NEE values, the lack of a relationship between these two variables in Campaign 1 shows that the controls on CH₄ fluxes are probably complicated and may vary inter-annually.

In summary, daytime-only measurements can lead to an underestimation of CH₄ fluxes, which may in turn cause underestimations of seasonal and annual estimates of CH₄ flux, and to GHG emission reporting required under the Kyoto Protocol. If countries are to develop higher tier emissions factors to improve on estimates from the IPCC, then diurnal variations in CH₄ fluxes should be considered, alongside prior land use and vegetation composition. Our study focusses on a peatland dominated by *Eriophorum* spp; similar studies will be needed on peatlands under restoration that are dominated by other types of vegetation.

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