The effects of peatland restoration on methane and carbon dioxide fluxes

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Abstract

Peatlands play an important role in the global carbon cycle. With rising levels of CO_2 and CH_4 in the atmosphere, a greater understanding of the controls on the flux of these gases from peatlands is important. In recent years, many peatlands have undergone restoration in attempts to reverse the damage caused by drainage. Therefore, the long-term effects of restoration on CO_2 and CH_4 fluxes are poorly understood. Peatland management strategies need to take the long-term responses of gaseous fluxes into account, and several hypotheses on these responses have been developed, despite the lack of data in this area.

Thorne and Hatfield Moors, two lowland raised bogs in Eastern England were subjected to drainage and peat extraction over several centuries. Restoration has occurred in stages on these peatlands (1997, 2003-2005, 2008), and there is also an area where restoration has not yet occurred, providing an excellent space-for-time substitution. Data showed that CH_4 fluxes were significantly larger at the two older sites in comparison to the younger site. Net ecosystem exchange and values of global warming potential were all positive (release to the atmosphere), and on average were larger at the two older sites in comparison with the unrestored site.

Diurnal variations in gaseous fluxes were also explored. Methane fluxes were significantly larger at night-time from areas dominated by *Eriophorum* spp., which suggests that CH_4 fluxes measured during the daytime could be underestimations. Carbon dioxide fluxes measured at night-time were larger than any of the daytime measurements of ecosystem respiration, where night-time conditions were simulated using a shroud to block the light. Therefore, ecosystem respiration measurements taken during the daytime could be underestimations. *Sphagnum cuspidatum* samples showed no evidence of a symbiosis with methanotrophs. Neither drought nor submergence of the *Sphagnum* sub-samples had any

significant effect on rates of methanotrophy. However, drought had a significant effect on rates of methanogenesis, with higher rates from sub-samples that had been allowed to dry out.

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Chapter 1: Introduction

1.1 Research overview

The research presented in this thesis is concerned with how fluxes of methane (CH_4) and carbon dioxide (CO_2) from peatlands may change with time following peatland restoration. Peatlands are significant reservoirs of carbon (C), and store more carbon than any other terrestrial organic carbon store (Immirzi et al., 1992). Many peatlands have been drained to make the land suitable for other purposes, such as agriculture (Bowler, 1980) or forestry (Cannell et al., 1993), or to extract the peat for use as fuel or in horticulture (Bonn et al., 2009). However, more recently, land managers have started to restore peatlands by raising the water table back to near the peat surface (Komulainen et al., 1999). Although raising the water table of a peatland can decrease CO_2 release to the atmosphere and increase carbon sinks (Kivimäki et al., 2008), the potential concurrent increase in CH_4 production and release to the atmosphere may counteract the overall reduction in C emissions when considered in terms of global warming potential (GWP) (Baird et al., 2009). Gaseous fluxes from peatlands are important with regards to climate change and efforts to reduce the impact of the enhanced greenhouse effect. Levels of atmospheric CO_2 and CH_4 are rising (Ciais et al., 2013; Dlugokencky et al., 2011), and in order to try and reduce these rises many countries have signed the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC); signatories must reduce their greenhouse gas emissions (United Nations, 1998). The UK is one of the signatories, and recently submitted its National Inventory Report for 1990-2012, where it was reported that since 1990 CO_2 emissions have been reduced by 20 % to 475.7 Mt, and CH_4 emissions by 51 % to 50.8 Mt CO_2-equivalent (Webb et al., 2014).

In 2008 the Climate Change Act was introduced as part of UK law, imposing a legally-binding GHG emission reduction target of 80 % below the 1990 base level to be achieved by 2050 (Webb et al., 2014). In order to assess the progress towards the achievement of this emission reduction target, the UK GHG Inventory exists, following UNFCCC guidelines from the Intergovernmental Panel on Climate Change (IPCC) (Thomson et al., 2012; Webb et al., 2014). There are six sectors to the Inventory: Energy, Industrial Processes, Solvent and Other Product Use, Agriculture, Land Use, Land Use Change and Forestry (LULUCF), and Waste, with wetlands included in the LULUCF sector (Webb et al., 2014). Thomson et al. (2012) reported a lack of inclusion the LULUCF section of the UK GHG Inventory with relation to managed peatlands. Methane emissions from rewetted organic soils and the land management technique of peatland drainage were not included in the guidance from the IPCC (Thomson et al., 2012). Recently, the IPCC (2014) published a wetlands supplement to their 2006 guidelines for National GHG Inventories. New inclusions include guidance on estimating GHG emissions from rewetted organic soils, and estimating CH_4 emissions from drained organic soils (IPCC, 2014).

The majority of studies into the effects of peatland restoration on CO_2 and CH_4 exchanges with the atmosphere occur within ten years of restoration starting (Cooper et al., 2014; Glatzel et al., 2004; Soini et al., 2010; Wilson et al., 2009). However, with the increasing focus on climate change mitigation, the longer-term response of peatlands to restoration in terms of gaseous fluxes is increasingly important. Despite the current lack of evidence in this area, policies are still being developed for peatland management over longer timescales (20-40 years). For example, Bain et al. (2011) hypothesised that within one to 10 years after restoration starts, the GWP of the peatland will fall, while between 10 and 20 years post-restoration the GWP should be negative (Bain et al., 2011). Joosten et al. (2006) presented a hypothesis that was adopted into peatland management strategies in Belarus. In this hypothesis, Joosten et al. (2006) proposed that within five-50 years of peatland restoration starting, after an initial spike, the GWP of the peatland would become negative (net cooling effect) and then reach an

equilibrium. The studies on which this hypothesis was based only included peatlands that had been restored for a maximum of seven years, and only one of the studies included restoration over this timescale (Waddington et al., 2001); the peatlands in the other studies had all been restored for shorter periods of time. Data to represent peatlands restored over a longer time period were taken from studies of undamaged peatlands (Augustin et al., 1996; Whiting and Chanton, 2001) due to the lack of data over a timescale greater than seven years. It is as yet unknown if restored peatlands will eventually function again like undamaged peatlands do. Therefore, using data from studies on undamaged peatlands to represent peatlands restored over a long timescale is potentially inaccurate, and at present an unfounded assumption. Overall there is a lack of studies on the effects of changes with time of gaseous fluxes in restored peatlands, and so the research reported in thesis was carried out to address this knowledge gap.

1.2 Research questions

This research was designed to consider longer-terms effects of restoration on CO_2 and CH_4 fluxes from peatlands. Six research questions were developed, and are listed below along with a brief rationale and the approach taken for each. A fuller rationale for each question can be found in Chapter 2 of this thesis.

1. **Do CH_4 and CO_2 emissions from peatlands change with time following restoration?**

As outlined above, there is a lack of research on gaseous fluxes from peatlands that have been restored over long timescales (in excess of seven-10 years). Despite this knowledge gap, peatland management policies are being developed over much longer timescales (20-40 years), and hypotheses have been developed that predict a reduction in GWP of restored peatlands with time using data from undamaged peatlands as a basis for long-term restoration conditions. Therefore, the work to address research question 1 will explore the effects of peatland restoration on

gaseous fluxes at sites that have been restored for up to 15 years. The field sites chosen for this study were Thorne and Hatfield Moors; two lowland raised bogs in eastern England. Peat was extracted from these sites over hundreds of years, and peatland restoration began in stages across the sites, providing a space-for-time substitution in which to study the temporal effects of restoration.

2. **What are the main drivers of CH_4 and CO_2 emissions in restored peatlands?**

If fluxes of CH_4 and CO_2 do change with time following restoration, it is important to know what is driving these changes. More information on the potential changes in gaseous flux drivers with time following restoration would be useful for land management decisions. For example, if a successional change in vegetation cover were causing higher CH_4 emissions, land managers could then take measures to reduce the growth of the plant type in question. Therefore, to address research question 2, the potential drivers of CH_4 and CO_2 emissions will be examined in the different-aged areas of Thorne and Hatfield Moors.

3. **Do CH_4 emissions vary diurnally, and if so, what are the main drivers of the diurnal variations?**

In many cases, field measurements of CH_4 fluxes from peatlands are conducted only during daylight hours, due to the use of manually-operated equipment. Measured fluxes are often used to calculate seasonal or annual fluxes, which are useful to land managers and policy developers for assessing peatland responses to land use change. Diurnal variation in CH_4 fluxes has been studied by many researchers; however, the results presented in the literature show varying results. For example, Mikkelä et al. (1995) showed that the diurnal CH_4 flux pattern was dependent upon the plant assemblages; yet, there has only been more than one or two studies conducted on the same vegetation type. Therefore, the work to address research question 3 will explore the diurnal variation in CH_4 fluxes to see if the fluxes measured during the daytime are representative of a 24-hour period.

4. **Does the diurnal variation in CO_2 emissions result in positive or negative net ecosystem exchange (NEE)?**

To measure the ecosystem respiration component of NEE, a commonly-used technique is to simulate night-time conditions through the use of a shroud to block out the light. However, other environmental variables that change at night, for example air temperature, are not accounted for. If this method does not accurately simulate all aspects of night-time conditions, then the ecosystem respiration component of NEE calculations could be over- or underestimated, which would then have a knock-on effect on GWP calculations. Therefore, the work for research question 4 will examine CO_2 fluxes in night-time and daytime conditions to see if measurements of ecosystem respiration are accurately representing real night-time conditions.

5. **Does drought affect methanotrophic activity within *Sphagnum* mosses?**

Methanotrophs are bacteria that use CH_4 as their sole energy and carbon source; they oxidise CH_4 into CO_2 through a process known as methanotrophy (Dedysh, 2002; Le Mer and Roger, 2001). Methane emissions from peatlands dominated by *Sphagnum* mosses are often lower than from areas where other vegetation types are dominant (Bowes and Hornibrook, 2006; McNamara et al., 2008; Parmentier et al., 2011). Vascular plants have aerenchymous tissues that can aid CH_4 transport out of deeper peat layers to the atmosphere, and their root exudates can encourage CH_4 production (Rydin and Clymo, 1989); however, methanotrophs are frequently found to reside within *Sphagnum* mosses, often within the hyaline cells (Kip et al., 2010; Raghoebarsing et al., 2005). The relationship between methanotrophs and *Sphagnum* can be mutually beneficial; photosynthesis within the mosses produces oxygen (O_2), which can be used by the methanotrophs to oxidise CH_4, and the CO_2 produced during methanotrophy can be used by the *Sphagnum* mosses for photosynthesis (Putkinen et al., 2012). Some authors have used the term 'symbiosis' to describe the mutually-beneficial relationship between methanotrophs and *Sphagnum* mosses (Raghoebarsing et al., 2005), and whilst it is

recognised that this is not the correct use of symbiosis in the absolute sense, the word has been used in this study to maintain compatibility with the literature.

The main aim of peatland restoration is to raise the water-table position (WTP) back to near the peat surface. However, it is not always possible to maintain this desired WTP, and so *Sphagnum* mosses that grow on a restored peatlands may be subjected to periods of drought. Drought can affect the photosynthetic abilities of *Sphagnum* mosses (Demmig-Adams and Adams, 1992; Harris, 2008), but it is unclear if drought has any effects on the hyaline cells, or the abilities of methanotrophs to function. Therefore, the work to address research question 5 will focus on determining rates of methanotrophy from *Sphagnum* mosses subjected to drought.

6. **Does submergence affect methanotrophic activity within *Sphagnum* mosses that have been subjected to drought?**

The mutually-beneficial relationship between methanotrophs and *Sphagnum* mosses, as described above, is reported to be at its strongest when *Sphagnum* mosses are submerged (Kip et al., 2010). However, it is unknown if the potential effects of drought, as explored in research question 5, have any effect on this relationship. Therefore, the work for research question 6 will examine if drought affects this mutually-beneficial relationship in submerged *Sphagnum* mosses.

1.3 Research approach

Measurements of gaseous fluxes were required in areas of Thorne and Hatfield Moors where restoration had started at different times. Fieldwork was conducted over 13 months and involved measuring fluxes of CH_4 and CO_2 on sites of three different ages and at a fourth site where restoration has not yet taken place (control site) to address research question 1. Fieldwork also involved measuring

water-table positions from dipwells and taking soil temperature readings, as well as collecting meteorological data using an automatic weather station. These data were needed to address research question 2. Fluxes measured during chamber sampling were scaled to seasonal and annual fluxes of CH_4 and net ecosystem CO_2 exchange. Through expressing CH_4 fluxes as CO_2-equivalents, GWP values were calculated.

To address research questions 3 and 4, a field campaign where gaseous flux measurements were taken at regular intervals over a 24-hour period was required. In July 2012 this field campaign occurred at one site on Thorne Moors where tests were conducted every 90 minutes over 24 hours to collect gaseous samples to be analysed for their CO_2 and CH_4 concentrations. The resulting fluxes from the 16 sets of tests were then analysed for their diurnal variation.

Research questions 5 and 6 required a mesocosm laboratory-based experiment using *Sphagnum* sub-samples which were subjected to different treatments of drought and submergence. The data were then used to calculate fluxes and the results from the different treatments were compared to see if drought and submergence had any effects on methanotrophy within *Sphagnum* mosses.

1.4 Thesis structure

This thesis comprises seven chapters. Chapter 2 presents a review of the relevant literature and identifies research gaps concerning the effect of restoration on the C balance of peatlands. The research gaps are used to identify the six research questions around which this research project was based. Chapter 3 describes the field sites, field equipment and methods, along with the analytical methods used. Research questions 1 and 2 are addressed in Chapter 4, where annual and seasonal fluxes of CO_2 and CH_4, as well as values of GWP are presented. The implications of

the findings for peatland management are also discussed in this chapter. Chapter 5 presents the study into the diurnal variation of CH_4 fluxes and net ecosystem CO_2 exchange, and therefore addresses research questions 3 and 4. The details of the laboratory-based experiment into the effects of drought and submergence on methanotrophy within *Sphagnum* mosses and the results thereof are found in Chapter 6. Chapter 7 is the final chapter and draws together all of the findings from the three results chapters, and the implications for peatland management as a result of these findings. Limitations of this work as well as suggestions for further work that would provide further insight into the findings of this research are presented here.

Chapter 2: Managing peatlands as carbon stores

2.1 Carbon cycling and climate change

2.1.1 The greenhouse effect

The Earth's climate is controlled by the balance between the solar energy absorbed from the Sun and the thermal infrared radiation emitted from the Earth (Shine et al., 1990). Greenhouse gases (GHGs) occur naturally within the atmosphere, and absorb considerable quantities of the infrared radiation emitted from the Earth (Jain, 2009). The presence of these GHGs has a warming effect and increases the Earth's surface temperature by 30-40 °C compared to if they were absent, and this warmer surface temperature allows life to exist (Barry and Chorley, 2002; Jain, 2009). In the natural greenhouse effect, water vapour (H_2O) is the main contributor, followed by carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) (IPCC, 1990). Increased levels of GHGs due to anthropogenic activities, particularly since the start of industrial times *circa* 1750, have enhanced this natural greenhouse effect, causing the Earth's surface temperature to rise (Jain, 2009). Generally, this rise in GHG concentrations in the atmosphere is deemed to be the cause of climate change with associated negative effects which include: melting ice sheets, glaciers and permafrost and rising sea levels; and more extreme seasons increasing flood risk and drought (Eggleton, 2012; IPCC, 2007).

The effects of different GHGs on climate can be expressed through the concept of radiative forcing. Radiative forcing quantifies the impact that a factor, such as a GHG, has on the Earth's climate, and allows factors to be compared with each other in terms of their effect on climate (IPCC, 2007). Positive radiative forcing indicates a warming effect, and negative radiative forcing indicates a cooling effect (IPCC, 2007). Global warming potential (GWP) is the time-integrated radiative forcing caused by a pulse emission of a gas relative to a pulse emission of the same

mass of CO_2 over a given time period, and so takes into account the absorption strength and atmospheric lifetime of a gas molecule along with its molecular weight and the time period of interest (Lashof and Ahuja, 1990; Shine et al., 1990; Shine et al., 2005). Global warming potentials are often expressed over time periods of 20, 100 and 500 years (Shine et al., 1990).

2.1.2 Carbon dioxide in the atmosphere

Levels of CO_2 in the atmosphere, which were approximately 280 parts per million volume (ppmv) in pre-industrial times (pre 1750), had increased to 353 ppmv by 1990 (Watson et al., 1990), and on May 9th 2013 was reported to have reached a daily average of 400.03 ppm; the first daily average above 400 ppm since recording began in 1958 (Showstack, 2013). Carbon dioxide contributed 61 % of the radiative forcing that has occurred over the last two centuries, making CO_2 the most important contributor to the enhanced greenhouse effect (Shine et al., 1990). Although CO_2 only remains in the atmosphere for approximately four years, due to the carbon cycle, the adjustment time for the atmosphere to respond to changes in the balance between sources and sinks of CO_2 is on the scale of 50 – 200 years (Watson et al., 1990). Given that it is the baseline for comparisons, the GWP for CO_2, over any time period, has a value of one (Shine et al., 1990). Also, because other gases are being compared to CO_2 using the GWP method, concentrations or fluxes of other gases are often reported as CO_2 equivalents (CO_2-e) (IPCC, 2007).

2.1.3 Methane in the atmosphere

Levels of CH_4 in the atmosphere were approximately 0.8 ppmv in pre-industrial times, rising to 1.72 ppm by 1990 (Watson et al., 1990), and by 2009 were reported at 1.79 ppm (Dlugokencky et al., 2011). In 2007, after almost a decade of stability, atmospheric CH_4 concentrations began to rise; by 0.008 ppm in 2007 and 0.006 in 2008 (Bousquet et al., 2011; Dlugokencky et al., 2009). Although Dlugokencky et al. (2009) were not certain on the causes of this renewed rise, increased emissions

from northern wetlands due to warm temperatures in 2007, increased emissions due to biomass burning in the tropics in October and November 2006, and increased emissions from tropical wetlands due to a La Niña event are all cited as possible contributors (Dlugokencky et al., 2009).

In terms of radiative forcing, CH_4 made the second largest contribution of the GHGs to radiative forcing over the last two centuries at 17 % (Shine et al., 1990). Although CH_4 is present in the atmosphere in much lower quantities than CO_2, each CH_4 molecule absorbs infrared radiation much more intensely than each molecule of CO_2 (Lashof and Ahuja, 1990). Methane emitted from the Earth's surface can be destroyed in the troposphere through oxidation by hydroxyl radicals (OH), where:

$$CH_4 + OH \rightarrow H_2O + CH_3$$

(Cicerone and Oremland, 1988). As much as 85 – 90 % of the CH_4 released into the atmosphere is oxidised through this reaction with OH (Cicerone and Oremland, 1988; Curry, 2007). The remaining 10 – 15 % of CH_4 emissions are either transported from the troposphere into the stratosphere, where they are destroyed by OH or chlorine (Cl) atoms, or are removed from the atmosphere through consumption by bacteria in soils in oxic conditions (Cicerone and Oremland, 1988; Curry, 2007). The atmospheric lifetime of CH_4 has been cited as approximately 8-10 years (Dlugokencky et al., 1998; Khalil and Rasmussen, 1983; Watson et al., 1990). However, more recent analysis has taken the feedback mechanism between CH_4 and OH into consideration. Myhre et al. (2013) define an emission impact from the relationship between CH_4 and OH, in that through its oxidation of CH_4, OH concentrations in the atmosphere are reduced. This reduction in OH concentrations thereby increases the atmospheric lifetime of CH_4 because there is less OH to break down CH_4 and remove it from the atmosphere (Myhre et al., 2013). By taking this feedback mechanism into account, the atmospheric lifetime

of CH_4 can be increased to 12.4 years (Myhre et al., 2013). Based on this atmospheric lifetime of 12.4 years, over a 20 year time horizon the GWP of CH_4 is 84, and over a 100 year time horizon the GWP is 28 (Myhre et al., 2013). Therefore, relative to CO_2, the same quantity of CH_4 has an effect on radiative forcing that is 28 or 84 times greater than CO_2 due to its stronger absorption of radiation depending on the timescale (Myhre et al., 2013).

In terms of predicting future climate change, the IPCC uses a modelling approach, but highlights that, in terms of CH_4 emissions, there are very few observational datasets upon which to base their predictions (Ciais et al., 2013). Therefore, the more observational datasets that are gained on CH_4 emissions from any environment the better for future climate change prediction models.

The Kyoto Protocol is an international agreement that calls for the signatory countries to reduce their GHG emissions, with specific targets over specific time periods (United Nations, 1998). Developed countries have higher emission reduction targets placed on them, because the industrial activities in these countries have made a greater contribution to the current GHG levels than developing countries (United Nations, 1998). Although the main focus of these emission reduction targets are anthropogenic sources, any measures that can be taken to enhance knowledge on the natural sinks and sources of GHGs, particularly CO_2 and CH_4, will benefit future emission reduction strategies.

2.2 Peatlands and the carbon cycle

2.2.1 Peatland carbon storage

Peatlands have been classified as areas where peat deposits are in excess of 30–40 cm in depth (Charman, 2002; Clymo, 1983). There are two main types of peatland, which can be broadly separated through differences in water supply and trophic

status (Lai, 2009). Ombrotrophic peatlands (bogs) receive water and nutrients mainly from precipitation, whereas minerotrophic peatlands (fens) also receive inputs from groundwater (Gorham, 1991; Wheeler and Shaw, 1995). Therefore, ombrotrophic bogs are more acidic and nutrient-poor, whilst minerotrophic fens are more likely to be alkaline and nutrient-rich (Charman, 2002). However, fens can be sub-classified as oligotrophic (nutrient-poor) and eutrophic (more alkaline and calcium-rich) (Charman, 2002). Yet there can be confusion as to the criteria required to distinguish one type of fen from another (Charman, 2002). Bogs can be sub-classified into blanket bogs and raised bogs; blanket bogs cover the landscape, whereas raised bogs have a convex-upward or domed profile (Charman, 2002).

Peatlands are a major component in the global carbon cycle (Ström et al., 2005; Ström and Christensen, 2007). In terms of terrestrial organic carbon stores, peatlands store the greatest amount of carbon, despite covering only approximately 3 % of the Earth's surface (Immirzi et al., 1992), which is around 4500000 km^2 (Blodau et al., 2004). On a global scale only oceanic deposits store more carbon (Joosten and Couwenberg, 2008). Peatlands can be found on every continent (Joosten, 2009), but are particularly prevalent in the northern hemisphere where they store an estimated 455-621 Gt C (Yu et al., 2010). Within Europe peatlands cover just less than 1900000 km^2 of land (Bragg, 2002), 14200 km^2 of which are found in England, covering 11 % of the land area (Natural England, 2010).

Storage in UK peatlands is estimated to be 2302 Mt C (Billett et al., 2010), of which approximately 584.4 Mt C is stored in English peatlands (Natural England, 2010). Table 2.1 shows the distribution of this storage within the different peatland types in England and the percentage of land area covered by each of the peatland types. Carbon can be released from a peatland in gaseous form as CO_2 or CH_4, in dissolved form as organic or inorganic carbon (DOC or DIC), or as particulate organic carbon

(POC) (Billett et al., 2010; Joosten and Couwenberg, 2008); however, this thesis will only focus on gaseous fluxes of carbon.

Table 2.1: Estimated total carbon storage in England's peat soils (adapted from Natural England (2010))

Peatland type	**Mt C**	**% of total peatland carbon**	**% of land area covered by peatland type**
Blanket bog and upland valley mire	138	24	29.4
Raised bog	57.5	10	3
Lowland fens/reedbeds	330.4	57	23.9
Shallow peaty soils	58.5	10	43.7

2.2.2 Peatland drainage and restoration

2.2.2.1 Drainage purposes

Both in the UK and globally, many peatlands have been extensively modified in order to make the land more suitable for other purposes, such as forestry (Cannell et al., 1993; Laiho et al., 1999), flood alleviation (Chacinski and Harris, 1963), agriculture (Bowler, 1980; Kasimir-Klemedtsson et al., 1997), grouse habitats (Holden et al., 2004; Ludwig et al., 2008) and peat extraction for use as fuel or a growing medium for horticulture (Bather and Miller, 1991; Bonn et al., 2009; Cleary et al., 2005; Vasander et al., 2003). In order to prepare the peatland for a new land use, drainage is often the main management tool employed, and is a process that has been practised for centuries (Gottlich et al., 1993; Holden et al., 2004; Ramchunder et al., 2009). In Canada the most common reason for peatland drainage is to extract the peat for use in horticulture (Cleary et al., 2005). However, in Finland, peatland drainage is most commonly used for forestry, where

one quarter of the forested area of the country is located on peatlands, covering approximately 57000 km^2 (Laiho et al., 1999). The area drained for coniferous forest plantations in the UK over the latter half of the 20^{th} century covers approximately 5000 km^2 (Cannell et al., 1993). Drainage generally involves the construction of regularly-spaced ditches across a peatland. For Finnish peatlands drained for forestry, Laiho et al. (1999) indicate that a spacing of 30-40 m between ditches and a ditch depth of 0.7-0.9 m was used. Armstrong et al. (2009) reported that drainage ditches in the UK were usually 0.5 m deep and 0.5-0.7 m wide. However, drainage is not the only peatland land management technique; in UK upland peatlands heather burning is often employed to improve habitat for grouse (Ramchunder et al., 2009).

Natural England (2010) report that more than 99 % of deep peat (where the majority of peat is > 40 cm deep) in England is classed as damaged, with similar values reported for other European countries including Germany (Raeymaekers, 2006). Natural England (2010) also report that approximately 74 % of peatlands in England are subjected to damaging land management, with raised bogs in particular damaged through peat extraction for horticulture. Although peat extraction is no longer widespread, 16 % of raised bogs in England still have peat extracted from them (Natural England, 2010).

2.2.2.2 Restoration purposes

The effect of peatland drainage on carbon storage has led to many land managers moving to restore peatlands. However, carbon storage is not the only reason for restoration, with biodiversity and hydrology cited by Schumann and Joosten (2008), as the two other main aims of restoration. Many peatlands previously damaged are now included in areas under special conservation status in order to aid restoration and prevent further damage (Raeymaekers, 2006). Peatlands are habitats for many invertebrate, bird and plant species; however, drainage can alter these habitats and therefore cause a reduction in the biodiversity (Wheeler and

Shaw, 1995). Restoring a damaged peatland to previous hydrological and biodiversity conditions may not be possible (Gorham and Rochefort, 2003). Firstly, the previous conditions for which to aim for with restoration may not be known (Gorham and Rochefort, 2003). Secondly, drainage can permanently damage the hydrological regime of a peatland due to the exposure of previously anoxic peat layers, changing the water storage capabilities and ultimately making it impossible to return the hydrology to a former 'pristine' state (Price, 1997; Schlotzhauer and Price, 1999). Alexander et al. (2008) indicated that a peatland that had been damaged could never be returned to its natural state, and that areas where peat extraction occurred via milling were more difficult to restore than block-cut areas due to the deeper drainage required for milling. Chapman et al. (2003) suggested that the spontaneous regeneration of peatland vegetation was harder to establish on areas that had been milled, and that block-cut areas could actually increase biodiversity by creating transition zones and re-establishing vegetation that had previously vanished due to successional changes. Wind-Mulder and Vitt (2000) conducted five years of monitoring on a natural peatland and a peatland where drainage and extraction had occurred. The damaged peatland was previously a bog, but had been returned to the fen-to-bog transition stage due to extraction, and so the peat and water chemistry were different to the original conditions (Wind-Mulder and Vitt, 2000). Haapalehto et al. (2011) studied a peatland that had originally been drained for forestry and was then restored through drain-blocking and deforestation, with a neighbouring undamaged area. Ten years after restoration started, the peat chemistry in the restored area was comparable with ><Year>2011</Year><RecNum>262</RecNum><DisplayText>Samaritani et al. playText><record><rec-number>262</re(Haapalehto et al., 2011). Andersen et al. (2006) suggested that biodiversity in terms of vegetation is likely to recover post-restoration faster than the biodiversity of the microbial community within a peatland. In terms of defining restoration success, Andersen et al. (2010) indicated that success might only be achieved once vegetation established post-restoration has been through its life cycle and becomes part of the peatland anoxic zone.

2.2.2.3 Gaseous dynamics

Peatlands that have been damaged through drainage are sources of CO_2 (Moore and Knowles, 1989; Silvola et al., 1996; Waddington et al., 2002; Waddington et al., 2010), with CH_4 emissions often at low or negligible rates (Alm et al., 1999; Martikainen et al., 1995; Moore and Roulet, 1993; Nykänen et al., 1998). Carbon dioxide dynamics in peatlands will be addressed in more detail in section 2.3. In brief, as shown in Figure 2.1a, carbon is effectively stored in peatlands through dead organic matter being subjected to anoxic conditions, where decomposition rates are much slower than in oxic conditions (Joosten and Couwenberg, 2008). However, if peatlands are drained, the extent of the anoxic zone shrinks, exposing more dead organic matter to oxic conditions, and therefore faster rates of decomposition which leads to higher CO_2 emissions (Sirin and Laine, 2008). Approximately 1 Gt C yr^{-1} in the form of CO_2 is emitted from drained peatlands globally, with English peatlands contributing approximately 3 Mt CO_2-e yr^{-1} (Natural England, 2010). More detail will be presented on CH_4 dynamics in section 2.4. In brief, as shown in Figure 2.1a, CH_4 is produced through the decay of peat and plant litter through a process called methanogenesis, which occurs in anoxic environments (Williams and Crawford, 1984). Root exudates from plants can be used as a source of energy for methanogenesis (Holzapfel-Pschorn et al., 1986). Methane can be transported out of the peat to the atmosphere by three pathways: diffusion; through the aerenchymous tissue of vascular plants; or by ebullition (bubbles of free-phase gas) (Frenzel and Rudolph, 1998). However, in the oxic zone there are bacteria than consume CH_4 called methanotrophs; therefore, CH_4 transported via diffusion or ebullition may never escape the oxic zone to the atmosphere (Segers, 1998). There may also be localised methanotrophy in the rhizosphere, because O_2 may be transported via aerenchyma from the atmosphere down the roots of vascular plants (Joabsson et al., 1999). In a drained peatland, as shown in Figure 2.1a, CH_4 emissions are reduced, due to a smaller anoxic zone for methanogenesis and a larger oxic zone for methanotrophy (Lai, 2009).

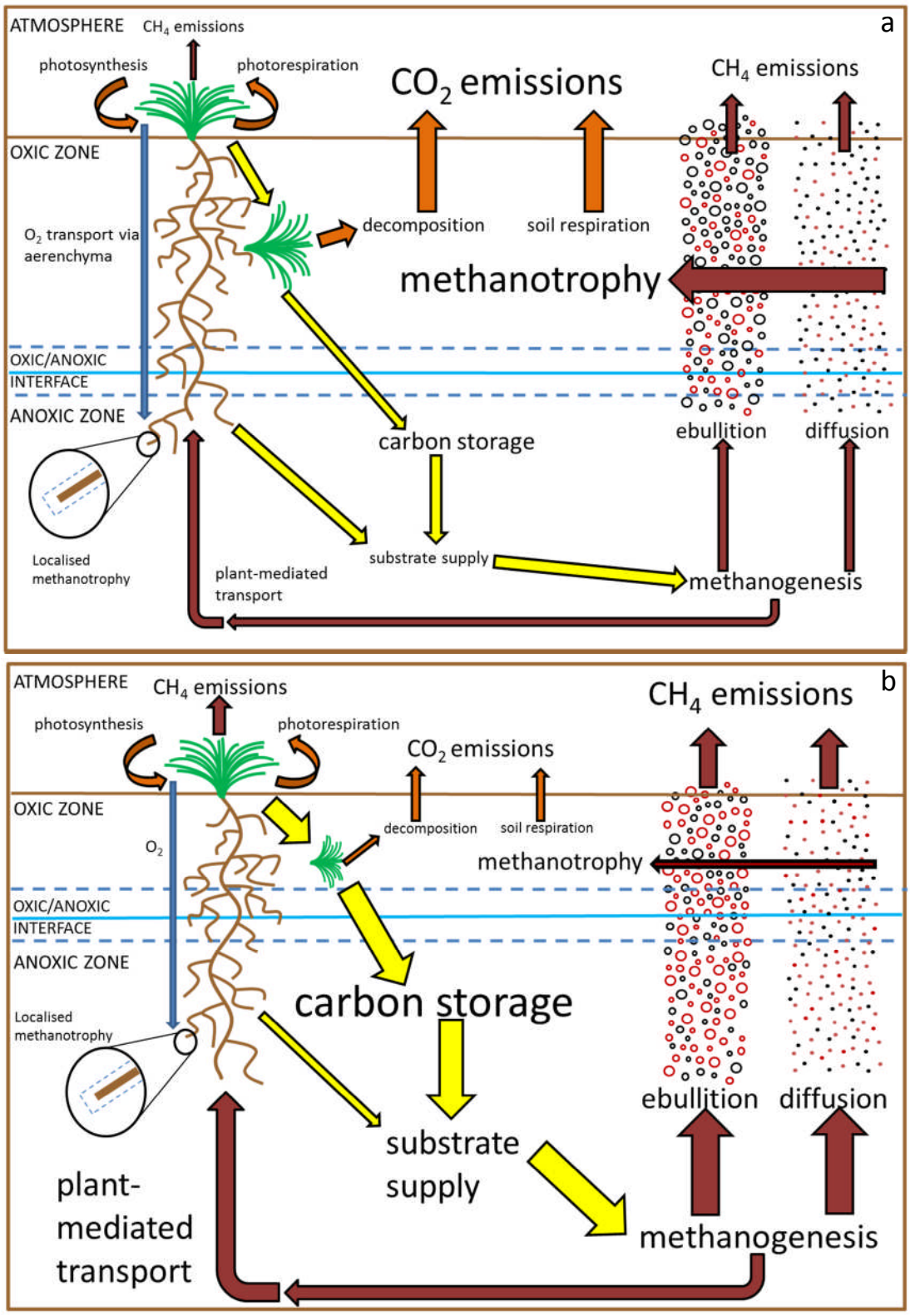

Figure 2.1: Conceptual diagrams of CO_2 and CH_4 dynamics in (a) a drained peatland and (b) a restored peatland. Larger font size or arrow widths indicate more prevalent processes.

A raised water-table position as a peatland restoration technique, should alter CO_2 and CH_4 dynamics, as shown in Figure 2.1b in the following ways. The anoxic zone increases in size, which increases the carbon storage potential. A larger anoxic zone will be able to store greater amounts of dead organic matter, slowing down the decomposition process and therefore storing the carbon within; however, a larger anoxic zone also increases the potential for methanogenesis. Greater amounts of dead organic matter will provide a larger energy source for methanogens to consume and produce CH_4, which suggests more CH_4 will be produced. A raised water-table position also results in a smaller oxic zone, which should lead to a reduction in CO_2 emissions, through less dead organic matter subjected to oxic conditions where decomposition can occur. Soil respiration rates should also be reduced through a smaller oxic zone, leading to further reductions in CO_2 emissions. Methanotrophs will have a smaller habitat within a thinner oxic zones, which will increase the amount of CH_4 that can escape through the oxic zone via diffusion or ebullition from the deeper anoxic layers into the atmosphere. The existence of these processes are generally agreed upon in a number of peatland carbon cycling reviews (Blodau, 2002; Lai, 2009; Le Mer and Roger, 2001; Limpens et al., 2008).

The peatland surface left behind following drainage will determine the role of vegetation in CO_2 and CH_4 dynamics when restoration through a raised water-table position occurs. In an area dominated by sedges where the roots extend into the anoxic zone, as shown in Figure 2.1b, the transport of CH_4 out of the deeper anoxic layers and into the atmosphere can be facilitated through aerenchymous tissues, increasing CH_4 emissions. Although, within the rhizosphere, increased O_2 supply, also facilitated by aerenchymous tissues, can lead to localised methanotrophy, which could reduce the amount of CH_4 that could escape via these plants. However, root exudation is a source of energy for methanogens, which can lead to increased rates of methanogenesis. In an area dominated by *Sphagnum* mosses, CH_4 emissions could be reduced, in comparison with sedge-dominated areas, in two ways. Firstly, *Sphagnum* mosses do not have roots, and so cannot provide a

transport pathway for CH_4 out of the anoxic layers, or exudates for methanogens. Secondly, methanotrophs have been shown to reside within *Sphagnum* mosses due to a mutually-beneficial relationship (explored further in section 2.4.4 and Chapter 7); therefore, more methanotrophy can occur if *Sphagnum* mosses are populated by methanotrophs, reducing CH_4 emissions. Again, these processes are generally agreed upon in a number of peatland carbon cycling reviews (Blodau, 2002; Lai, 2009; Le Mer and Roger, 2001; Limpens et al., 2008). On a bare peat surface it will depend upon which species colonise the area first, as to which processes occur and what the balance between CO_2 and CH_4 dynamics are. Some restoration work, most commonly in North America, alongside raising the water-table position, has involved encouraging *Sphagnum* growth through spreading *Sphagnum* diaspores (Campeau and Rochefort, 1996; Rochefort et al., 2003).

Overall, the peatland restoration process can be seen as a balancing act between the contrasting gaseous dynamics. A reduction in CO_2 emissions and increased potential for carbon storage are often cited as a major benefit of peatland restoration (Kivimäki et al., 2008; Soini et al., 2010; Tuittila et al., 1999; Waddington et al., 2010). However, CH_4 is a more potent GHG in radiative forcing terms, as discussed in section 2.1, and so benefits gained from peatland restoration in terms of reduced CO_2 emissions may be offset, at least partly, by increased CH_4 emissions due to the larger anoxic and smaller oxic zones (Baird et al., 2009). Both Herbst et al. (2013) and Olson et al. (2013) studied CO_2 and CH_4 fluxes over three years (2009-2011) using eddy covariance at Skjern Meadows, Denmark and Bog Lake Fen, Minnesota, USA respectively. The results of both studies showed that each peatland was a carbon sink in each of the three years; -42 to -259 g C m^{-2} (Herbst et al., 2013) and -14.6 ± 21.5 to -26.8 ± 18.7 g C m^{-2} (Olson et al., 2013). However, when the GWP was taken into account on a 100-year time horizon, Herbst et al. (2013) found that the Skjern Meadows had a negative radiative forcing effect in 2009, a positive radiative forcing effect in 2010, and a neutral effect in 2011. Olson et al. (2013) found that the Bog Lake Fen had a positive radiative forcing effect in all three years respectively; 69, 83 and 187 g C m^{-2}.

2.2.2.4 Gaseous flux studies

Many studies that investigate the impact of peatland restoration on gaseous carbon fluxes take place less than ten years after restoration activities started (such as damming or blocking drainage ditches) (Badiou et al., 2011; Bortoluzzi et al., 2006; Cooper et al., 2014; Francez et al., 2000; Glatzel et al., 2004; Komulainen et al., 1998; Marinier et al., 2004; Tuittila et al., 1999). There are some studies on gaseous carbon fluxes that examine peatlands where restoration started approximately ten years prior to the study (Herbst et al., 2013; Kivimäki et al., 2008; Soini et al., 2010; Strack and Zuback, 2013; Wilson et al., 2007; Wilson et al., 2009). Only one study could be found where restoration started more than ten years prior to the research (Basiliko et al., 2007).

Many of these studies took place at sites where there were tens of years between the cessation of peat extraction and the start of restoration activities (Bortoluzzi et al., 2006; Cooper et al., 2014; Komulainen et al., 1998; Tuittila et al., 1999; Wilson et al., 2007; Wilson et al., 2009); however, Marinier et al. (2004) studied an area where restoration started only one year after peat extraction had finished. A common starting scenario in many of these studies was a previously cutover bog, with restoration through drain-blocking (Bortoluzzi et al., 2006; Glatzel et al., 2004; Kivimäki et al., 2008; Marinier et al., 2004; Tuittila et al., 1999; Wilson et al., 2007; Wilson et al., 2009). The restoration technique at the sites studied by Cooper et al. (2014) and Komulainen et al. (1998) was also drain-blocking, but the original drainage was to improve the land for grazing (Cooper et al., 2014) or forestry (Komulainen et al., 1998), not for peat extraction. In the studies by Francez et al. (2000) and Strack and Zuback (2013) dykes were created on the peatlands to hold back water to raise the water-table position.

Worrall et al. (2011) conducted a review of evidence on carbon fluxes and GHG emissions from UK peatlands, and reported a complete lack of UK-based studies that focussed on peatland restoration concerning GHG emissions; although, there

is now the study by Cooper et al. (2014). However, there are long-term studies in both the UK and Ireland on peatland gaseous carbon budgets from relatively undamaged peatlands. There has been intensive work on the carbon budget, both gaseous and aquatic, on Auchencorth Moss in Scotland (Dinsmore et al., 2009a; Dinsmore et al., 2009b; Dinsmore et al., 2010); however, although the Auchencorth catchment consists mostly of peat soils (85 % (Billett et al., 2004)), the area from which peat was extracted and was then restored is relatively small compared to the catchment size as a whole (Dinsmore et al., 2010). Dinsmore et al. (2009a) examined the effects of drainage and rewetting on peat cores in a laboratory setting. All three greenhouse gases (CO_2, CH_4 and nitrous oxide (N_2O)) were monitored, and overall CO_2 and N_2O emissions were highest at low water-table positions, and CH_4 emissions highest at high water-table positions, as would be expected. Dinsmore et al. (2009a) found cores containing aerenchymous vegetation produced the lowest CH_4 fluxes; in agreement with some studies (Bhullar et al., 2013; Roura-Carol and Freeman, 1999), but in disagreement with others (Greenup et al., 2000; Strack et al., 2006). Dinsmore et al. (2009b) focussed on variability in CH_4 and N_2O fluxes in a field experiment, and found the same pattern for CH_4 fluxes from areas with aerenchymous vegetation as Dinsmore et al. (2009a); however, an area dominated by *Juncus effusus* was a hotspot for CH_4 emissions (Dinsmore et al., 2009b). In the field study of Dinsmore et al. (2009b) the water-table position was not found to be a driving variable in all chambers measured; only those that did not contain aerenchymous vegetation. The work by Dinsmore et al. (2010) produced a complete carbon budget for the Auchencorth catchment and emphasised the importance of including aquatic as well as gaseous carbon fluxes in studies. The study took place over two years and found that the Auchencorth catchment was a net carbon sink (-352 g CO_2-e m^{-2} yr^{-1}). All of the CH_4 and N_2O fluxes measured (when reported as CO_2-e) only erased 4 % of the NEE uptake. In 2007 43.96 ± 12.06 g CO_2-e m^{-2} yr^{-1} was lost from aquatic sources, and 53.44 ± 18.94 g CO_2-e m^{-2} yr^{-1} in 2008 (Dinsmore et al., 2010). There has also been a long-term study at the Glencar blanket bog in Ireland, which has no reported artificial drainage (Koehler et al., 2011; Sottocornola and Kiely, 2010). Sottocornola

and Kiely (2010) reported on five years (2002-2007) of CO_2 fluxes measured by eddy covariance and found that the peatland was a carbon sink for all five years (average of -54.9 ± 15.6 g C-CO_2 m^{-2}), and that all of the negative NEE (CO_2 uptake) occurred between May and September during every year. Koehler et al. (2011) expand upon the previous study by reporting on six years (2003-2008) of total carbon fluxes (CO_2, CH_4 and DOC) from Glencar. Over the six years, the site was still a mean net carbon sink; CH_4 and DOC fluxes were positive overall (4.1 ± 0.5 g C m^{-2} yr^{-1} and 14.0 ± 1.6 g C m^{-2} yr^{-1} respectively), but were counteracted by CO_2 uptake (-47.8 ± 30 g C m^{-2} yr^{-1}) in four out of the six years (Koehler et al., 2011). Overall, as well as a paucity of long-term UK studies, there is a lack of information on the GWP of peatlands following restoration both in the UK and in general over a timescale of more than ten years (Baird et al., 2009).

2.2.2.5 Predicting the results of restoration

Despite the lack of studies into the long-term effects of restoration, land-management policies are still being based on the literature that is available, and on untested assumptions, such as in the following example. In Belarus, a project began with the aim of restoring 42 000 ha found over 17 drained peatlands (fens and raised bogs) (Joosten et al., 2006). Joosten et al. (2006) developed a hypothesis on the succession of CO_2-e emissions, and therefore GWP, from these Belarusian peatlands following restoration, as shown in Figure 2.2. In this hypothesis, immediately following restoration, the GWP of a peatland rises as a result of high CH_4 emissions and low CO_2 sequestration (phase 1), followed by a sharp decline caused by lowered CH_4 emissions and increased CO_2 sequestration (phase 2) and ending with an equilibrium of low rates of CH_4 emissions and CO_2 sequestration (Joosten et al., 2006).

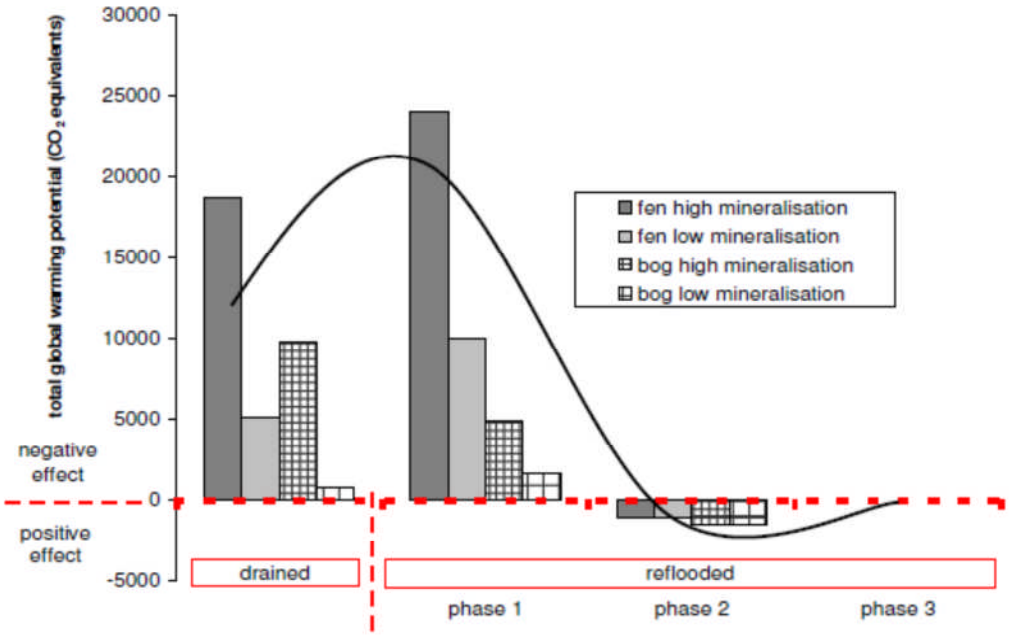

Figure 2.2: Estimated changes in total GWP of the GHG release from Belarusian peatlands following restoration (CO_2-e in units of kg ha^{-1} yr^{-1}). Taken from Joosten and Augustin (2006).

The basis for the data in Figure 2.2 comes from Augustin et al. (1996), Augustin et al. (1998), Kasimir-Klemedtsson et al. (1997), Laine et al. (1996), and Merbach et al. (2001) for drained peatlands prior to restoration; and from Komulainen et al. (1999), Petrone et al. (2001), Tuittila et al. (2004), Waddington and Price (2000), Waddington et al. (2001), Waddington et al. (2003) and unpublished data from the authors of Joosten et al. (2006) for peatlands that have been rewetted. Due to the lack of long-term post-restoration data, Joosten et al. (2006) used data from studies of natural or undamaged peatlands as a proxy of what the carbon balance of a long-term restored peatland will be like (Armentano and Menges, 1986; Augustin et al., 1996; Roulet, 2000; Whiting and Chanton, 2001), but had no supporting data to prove that restored peatlands would return to a natural state in the long term. As detailed earlier in this section, it may not be possible for a damaged peatland to return to its undisturbed state in terms of hydrology and biodiversity (Gorham and Rochefort, 2003; Price, 1997; Schlotzhauer and Price, 1999). Therefore, given the influence that water-table position and vegetation

cover can exert on gaseous flux dynamics (Blodau, 2002; Lai, 2009; Le Mer and Roger, 2001; Limpens et al., 2008), it is highly unlikely that a restored peatland will function the same as a natural peatland in terms of gaseous fluxes. Joosten et al. (2006) do not define what they classed as long term; however, upon examining the studies used by Joosten et al. (2006) for rewetted sites, the longest post-restoration study in that classification is seven years in the study by Waddington et al. (2001). Therefore, in this case, long-term post-restoration is assumed to be in excess of seven years.

As well as all of the studies cited above, Joosten et al. (2006) also had access to data on the Belarusian peatlands that were the subject of the restoration project, allowing the four classifications of fens and bogs with high and low mineralisation rates that can also be seen in Figure 2.2, and therefore the GWP values in Figure 2.2 are based on these 17 Belarusian peatlands. Using a time period of 100 years, Joosten et al. (2006) calculated three scenarios to estimate how long each of the phases shown in Figure 2.3 might last, although no information is provided on how the calculations were derived, or to what data they were applied. The best-case scenario has phase 1 lasting for only 5 years, phase 2 for 15 years and phase 3 for 50 years. In the worst-case scenario phase 1 is extended to 50 years, with phase 2 lasting for only 1 year and phase 3 for 49 years. Joosten et al. (2006) make no reference to what the environmental controls of CO_2 and CH_4 fluxes are, and what may change with these controls that would cause the shifts between the three phases outlined.

Bain et al. (2011) presented a similar hypothesis to that of Joosten et al. (2006) for UK peatlands. The hypothesis of Bain et al. (2011) is shown in Figure 2.3, where the data are described to be conservative estimates based on work by Billett et al. (2010), Byrne et al. (2004), Couwenberg et al. (2011), Holden et al. (2007), McNamara et al. (2008), Minkkinen et al. (2007), Silvola et al. (1996), Wallage et al. (2006), Worrall et al. (2010) and Worrall et al. (2011). Of these studies, four review

total carbon budgets in UK peatlands, including gaseous fluxes of CO_2 and CH_4 (Billett et al., 2010; Holden et al., 2007; Worrall et al., 2010; Worrall et al., 2011), and three focus on gaseous fluxes of CO_2 and CH_4 in Europe (including the UK) (Byrne et al., 2004), in Belarus (Couwenberg et al., 2011) and in the UK (McNamara et al., 2008). Both Minkkinen et al. (2007) and Silvola et al. (1996) studied CO_2 fluxes in Finland. Despite the UK focus of the work by Bain et al. (2011), perhaps studies not based in the UK were used to formulate the hypothesis due to a lack of UK-based studies on gaseous fluxes from restored peatlands. There are no gaseous fluxes in the study by Wallage et al. (2006), where the focus was DOC. Therefore, it is assumed that the net carbon fluxes shown in Figure 2.3 include non-gaseous fluxes.

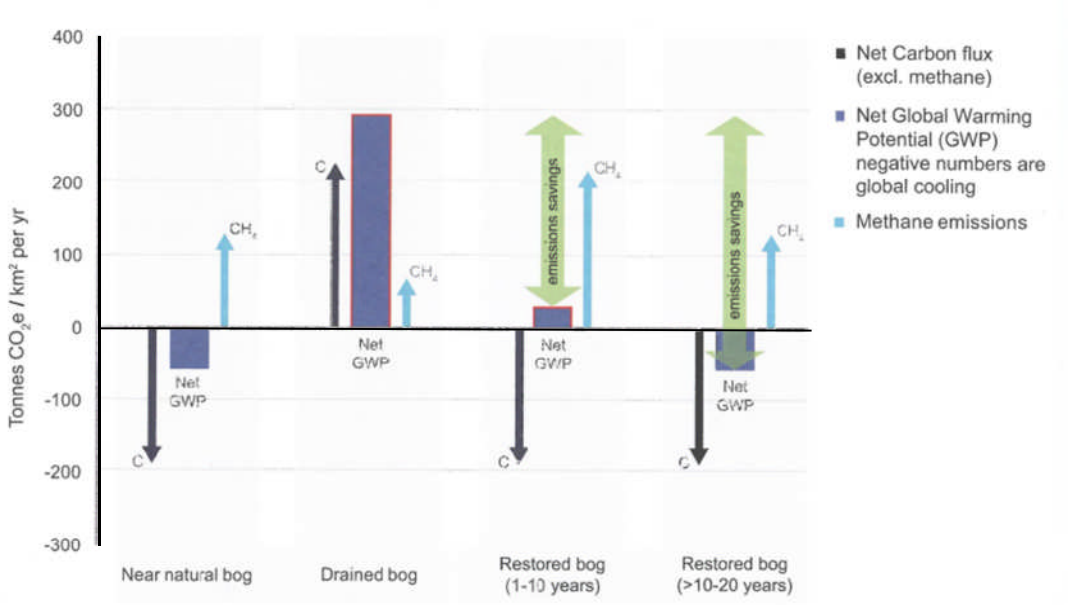

Figure 2.3: Estimated changes in GWP of UK peatlands under various stages of restoration. Taken from Bain et al. (2011).

The timescale for a restored UK peatland to switch from a source to a sink of carbon in the hypothesis of Bain et al. (2011) is different from the best-case scenario (phase 1) in the hypothesis of Joosten et al. (2006) for Belarusian peatlands. Bain et al. (2011) suggested that a restored peatland in the UK could

switch from a source to a net sink of carbon ten years after restoration started. However, this faster switch suggested by Bain et al. (2011) may be due to this hypothesis considering non-gaseous carbon fluxes, unlike Joosten et al. (2006).

Samaritani et al. (2011) studied net ecosystem CO_2 exchange (NEE) on a cutover bog in the Jura Mountains, Switzerland over one growing season on sites where cutting had stopped 29, 42 and 51 years previously. No active restoration work had occurred, but *Sphagnum* cover had re-established naturally (Samaritani et al., 2011). Through both measurements and modelling, Samaritani et al. (2011) found that the 29-year site was a net source of CO_2-C (40 g CO_2-C m^{-2}), whereas both the 42- and 51-year sites were net sinks, with respective average uptake rates of 222 and 209 g CO_2-C m^{-2}. These findings by Samaritani et al. (2011) support the hypothesis of Joosten et al. (2006), in that the post-cutting sites followed a similar pattern to the graph shown in Figure 2.3; a net source followed by a net sink. From a study on a peatland over one year prior and three years post restoration in Québec, Canada where drainage ditches had been blocked and *Sphagnum* fragments had been introduced to speed up re-vegetation, Waddington et al. (2010) hypothesised that it would take 6-10 years from restoration for the site to become a net carbon sink, which is similar to the hypothesis presented by Bain et al. (2011). A maximum of 10 years to become a net carbon sink (Waddington et al., 2010) is a much shorter timescale than observed by Samaritani et al. (2011); although the Canadian site was subjected to active restoration measures, unlike the Swiss site (Samaritani et al., 2011; Waddington et al., 2010).

The work by Samaritani et al. (2011) only accounted for CO_2 fluxes, whereas the hypotheses of Joosten et al. (2006) and Bain et al. (2011) consider both CO_2 and CH_4 fluxes. Although, of all of the published work cited by Joosten et al. (2006) to represent rewetted peatlands, only one (Waddington and Price, 2000) makes any reference to CH_4, with the rest of the studies only focussing on CO_2 (Komulainen et al., 1999; Petrone et al., 2001; Tuittila et al., 2004; Waddington et al., 2001;

Waddington et al., 2003). The hypothesis presented by Joosten et al. (2006) is based on data from 15 published sources, compared with ten published sources used by Bain et al. (2011); however, the work of Bain et al. (2011) is more thorough in that the majority of sources used studied both CO_2 and CH_4 fluxes. Although Joosten et al. (2006) used more published sources, and some unpublished data, scenarios are presented, as shown in Figure 2.2, for four different peatland types across three different potential time series, whereas the hypothesis presented by Bain et al. (2011), as shown in Figure 2.3, only relates to peat bogs. Given that some of the data used by Joosten et al. (2006) to formulate their hypothesis is unpublished, it is unknown what peatland types are included, and what gaseous emissions data was available to support the published data sources used.

Joosten et al. (2006) claim that the restoration planned in Belarus will reduce the GHG emissions from the peatlands there by approximately 0.2-0.4 million tons CO_2-e annually at the very least. However, the data on which this restoration policy in Belarus is based is from a hypothesis constructed with incomplete information on the long-term response of gaseous fluxes from post-restoration peatlands. The implementation of this policy in Belarus could mean that the predicted GHG emission reduction will be an over-estimation, especially because the hypothesis was based mainly on CO_2 flux data, with little use of data on CH_4 fluxes, despite the inclusion of CH_4 fluxes in the hypothesis. The reduction in CO_2-e emissions predicted from this rewetting programme for 42000 ha of peatlands in Belarus by Joosten et al. (2006) would greatly benefit the ability of Belarus to meet their commitments to the Kyoto Protocol. Yet, despite the cited lack of evidence to support the theory that a rewetted peatland will eventually revert back to behaving (in gaseous flux terms) like it once did prior to drainage, Joosten et al. (2006) still use this assumption in their study to predict the fate of the rewetting programme. It is recognised that land management practices still have to be designed and implemented, even when supporting evidence does not exist. Yet there are many changes that drainage can cause in peatlands, such as alterations to the peat structure which affects hydrology and the changes in vegetation compositions

between undisturbed, drained and rewetted peatlands, as discussed earlier in this section.

The data presented by Bain et al. (2011) was published several years after Joosten et al. (2006), yet there is no reference to Joosten et al. (2006) work in the relevant section of the Bain et al. (2011) work, which is surprising given that both deal with predicting how peatlands will respond to rewetting in the long-term in terms of gaseous fluxes. However, it is recognised that each publication deals with peatlands in different countries. Bain et al. (2011) do state that the data shown in Figure 2.3 is a potential, not a guaranteed result of rewetting, but also describe the data shown in Figure 2.3 as conservative, yet there is no mention of the lack of data on the responses of peatland gaseous fluxes over the 10 – 20 year period shown.

Therefore, more work focussing on gaseous fluxes, particularly CH_4, from restored peatlands is needed in order to better understand the long-term effects of restoration on these fluxes. Particular attention, where possible, would be beneficial on areas that have been restored in excess of seven years, as data on gaseous fluxes on these longer timescales is the area most lacking in the literature. Without more work in this area, the prediction of future GHG emissions, and therefore the GWP, from restored peatlands will be hard to calculate. A lack of accurate predictions of future GHG emissions from peatlands will also make it more difficult to quantify the impact that peatlands could have on the ability of a country to meet its Kyoto Protocol targets.

2.3 Carbon dioxide dynamics in peatlands

2.3.1 Net ecosystem CO_2 exchange

Net ecosystem CO_2 exchange is the balance between primary production and ecosystem respiration. Ecosystem respiration includes both plant and microbial (autotrophic and heterotrophic) respiration (Bubier et al., 2002). The main controls on NEE in peatlands are photosynthetically-active radiation (PAR), water-table position, and temperature (Humphreys et al., 2006; Lafleur et al., 2001; Lafleur et al., 2003; Moore et al., 1998). There are both seasonal and diurnal differences in NEE, due to the fact that these three main controls, particularly PAR and temperature, vary over these timescales (Bubier et al., 2003; Moore et al., 1998; Neumann et al., 1994). Whether peatlands are a sink or a source of CO_2 depends on balance between these processes, as shown in Figure 2.1. Although neither PAR nor temperature can be controlled, a thorough understanding of all three of these controls is important in terms of peatland management with relation to gaseous fluxes.

2.3.2 Primary production

Carbon storage in peatlands is initiated by plant photosynthesis. Although some CO_2 is returned to the atmosphere during photorespiration, the remaining carbon is stored as plant biomass (Sirin and Laine, 2008). Plant litter, when exposed to oxic conditions will lose some of this carbon storage as CO_2 to the atmosphere through organic matter decomposition; however, this litter may only be exposed to oxic conditions for a short amount of time, before transference to the anoxic zone (Joosten and Couwenberg, 2008; Sirin and Laine, 2008). Each year new litter is deposited on top of the material from the previous year (Belyea and Baird, 2006). Eventually the weight of the material above causes structural collapse in the material below, a process which is also aided by the material below losing structural strength due to decomposition (Belyea and Baird, 2006; Clymo, 1984). This structural collapse causes a decrease in the size of pore spaces and, therefore,

the hydraulic conductivity of the peat (Belyea and Baird, 2006; Clymo, 1984). Due to these decreases, the flow of water is hindered, therefore preventing the water table from falling below the point of the structural collapse (Belyea and Baird, 2006). Once below the water table, any remaining plant biomass is subjected to mainly anoxic conditions where decay may be orders of magnitude lower than in oxic conditions (Joosten and Couwenberg, 2008); however, only up to 16 % of the total primary productivity of peatland vegetation reaches this stage (Laiho, 2006; Päivänen and Vasander, 1994). Certain types of litter are more resistant to decay than others (Belyea, 1996). *Sphagnum* mosses have been shown to be more resistant to decay than vascular plants (Aerts et al., 1999; Frolking et al., 2001; Hobbie, 1996; Thormann et al., 2001). Anoxic decay is reported to occur at the highest rates just a few centimetres below the water table, but then with depth decreases by up to three orders of magnitude (Belyea and Clymo, 1998; Clymo and Bryant, 2008; Malmer and Wallén, 2004). Basiliko et al. (2007) found that both oxic and anoxic decay were constrained by organic matter quality; especially the carbon and phosphorus chemistry of the peat. One of the main results of anoxic decay is CH_4 production, which will be examined in more detail in Section 2.4.1.

2.3.3 Ecosystem respiration

Two of the main controls on the release of CO_2 from peatlands are water-table position and peat temperature. The position of the water table and therefore the extents of the oxic and anoxic zones are a major control on whether a peatland is a sink or source of CO_2 (Frolking et al., 2009; Sirin and Laine, 2008). A lower water table leads to greater CO_2 emissions through greater rates of decomposition caused by a larger oxic zone (Bubier et al., 2003; Hogg et al., 1992; Hooijer et al., 2010; Moore and Knowles, 1989), as shown in Figure 2.1a. However, Lafleur et al. (2005) found that temperature (r^2 = 0.62), but not water-table position (r^2 = 0.11) explained much of the variation found in ecosystem respiration on a temperate peatland. Temperature affects microbial activity and gas solubility; therefore, rising temperatures within a peatland may lead to higher CO_2 emissions, mainly

because of an increase in decomposition, but a reduction in gas solubility may also have a small effect (Sirin and Laine, 2008). It is reported that, on average, for every 10 °C rise in peat temperature, CO_2 emissions increase by a factor of two-to-three (Q_{10} = 2-3) (Blodau, 2002).

From a laboratory study using peat samples collected from a Canadian peatland dominated by *Picea mariana* (Mill.), Hogg et al. (1992) found that CO_2 emissions were greater from drained peat samples that from samples where a high water table was maintained. However, the study also found that CO_2 emissions only increased with decreasing saturation to a certain point. Once very low levels of saturation were reached, respiration rates decreased again (Hogg et al., 1992). The same study also concluded that with increasing moisture content, the effects of temperature on peat decomposition decreased, reducing Q_{10} values from 1.9 – 2.2 to 1.0 – 1.5 (Hogg et al., 1992). In contrast, Moore and Dalva (1993) found that the position of the water table (ranging from the peat surface to 40 cm below) had no influence on the effects of temperature on peat decomposition in their laboratory experiments. Additionally, Moore and Dalva (1993) observed that CO_2 emissions increased linearly when the water table was lowered from the surface of the incubated peat sample to a depth of 40 cm.

The position of the water table and temperature are affected by the changing seasons, so their effects of peat decomposition are also seasonal, with the greatest emissions occurring when temperatures are highest and water tables are lowest (Schaufler et al., 2010). Peatlands can exhibit highly variable NEE rates between different seasons and years (Aurela et al., 2009; Bubier et al., 2003; Christensen et al., 2012; Griffis et al., 2000; Lafleur et al., 2003; McVeigh et al., 2014; Nilsson et al., 2008; Roulet et al., 2007; Trudeau et al., 2014). Some studies found that, although there was variability, the overall NEE balance was negative (net CO_2 uptake) for every year studied, despite CO_2 emissions in the winter months (Aurela et al., 2009; Christensen et al., 2012; McVeigh et al., 2014; Nilsson et al., 2008; Roulet et al.,

2007); whereas others found that the direction of NEE flux changed between years (Griffis et al., 2000), or had a positive balance each year (Trudeau et al., 2014). The length of the growing season or the growth stage of the peatland vegetation was cited by many authors as having the strongest influence over the NEE balance (Aurela et al., 2009; Christensen et al., 2012; Griffis et al., 2000; McVeigh et al., 2014; Nilsson et al., 2008; Trudeau et al., 2014). McVeigh et al. (2014) reported that over ten years of study, years with a lower water-table position corresponded with the lowest values of CO_2 uptake, and that the one driest growing season month (May 2010) was the only period during which the NEE balance was positive during a growing season. Aurela et al. (2009) found that the lowest CO_2 uptake that occurred was a result of the warmest and driest conditions observed throughout the study period, which caused a reduction in plant photosynthesis and ecosystem respiration. Bubier et al. (2003) found differences in CO_2 flux between two summers, one wet, one dry. In the wet summer, temperature was the more accurate predictor of respiration, whereas in the drier summer the water-table position was the better predictor (Bubier et al., 2003). However, with weather conditions being so different during the two summers studied, Bubier et al. (2003) found increases in respiration to be the main cause of NEE change. The only changes (reductions) in photosynthesis were found at sedge-dominated sites; sites dominated by ericaceous shrubs only showed reduced rates of photosynthesis at the very end of the growing season in the drier summer (Bubier et al., 2003).

2.4 Methane dynamics in peatlands

In the northern hemisphere, the largest natural source of CH_4 is peatlands (Yu et al., 2009). Figure 2.4 shows the sources for both the total CH_4 flux from the Earth surface to the atmosphere (574 Mt CH_4 yr^{-1}), and flux from natural sources (238 Mt CH_4 yr^{-1}) (Reay et al., 2010). Both charts clearly show that wetlands are responsible for a large quantity of the total CH_4 flux and the majority of the natural CH_4 flux to the atmosphere (174 Mt CH_4 yr^{-1}) (Reay et al., 2010).

2.4.1 Methane production

Methane production occurs in the anoxic zone of a peatland. Peat and plant litter decay contribute to CH_4 production (Baird et al., 2009; Williams and Crawford, 1984). Methane is produced by archaea and a number of bacteria within a complex food web (Segers, 1998). There are two different methanogen groups within the archaea; one which ferments acetate or similar organic compounds to produce CH_4 and CO_2 (as shown below), and one that oxidises hydrogen (H_2) and reduces CO_2 to produce CH_4 (Gauci et al., 2004; Le Mer and Roger, 2001; Schimel, 2004).

The fermentation process responsible for producing CO_2 and CH_4, given by:

$$C_6H_{12}O_6 \rightarrow 3\ CO_2 + 3\ CH_4$$

is dependent upon the consecutive actions of four microbial populations (Le Mer and Roger, 2001). These actions are: hydrolysis, acidogenesis, acetogenesis and, finally, methanogenesis (Le Mer and Roger, 2001). Acetate fermentation may be responsible for more than 67 % of CH_4 production, with the oxidation of H_2 and the reduction of CO_2 responsible for the remaining 33 % (Kotsyurbenko et al., 2004). However, the relative contributions of these two different methanogen groups may vary with increasing depth through the peat profile. The contribution of H_2-oxidising and CO_2-reducting methanogens increases with depth to 50 – 100 % of CH_4 production (Kotsyurbenko et al., 2004). Bellisario et al. (1999) indicated that acetate fermentation was the more dominated method of CH_4 production in vegetated areas due to the input of fresh organic matter, with areas dominated by recalcitrant material were more likely to rely on CO_2 reduction for methanogenesis.

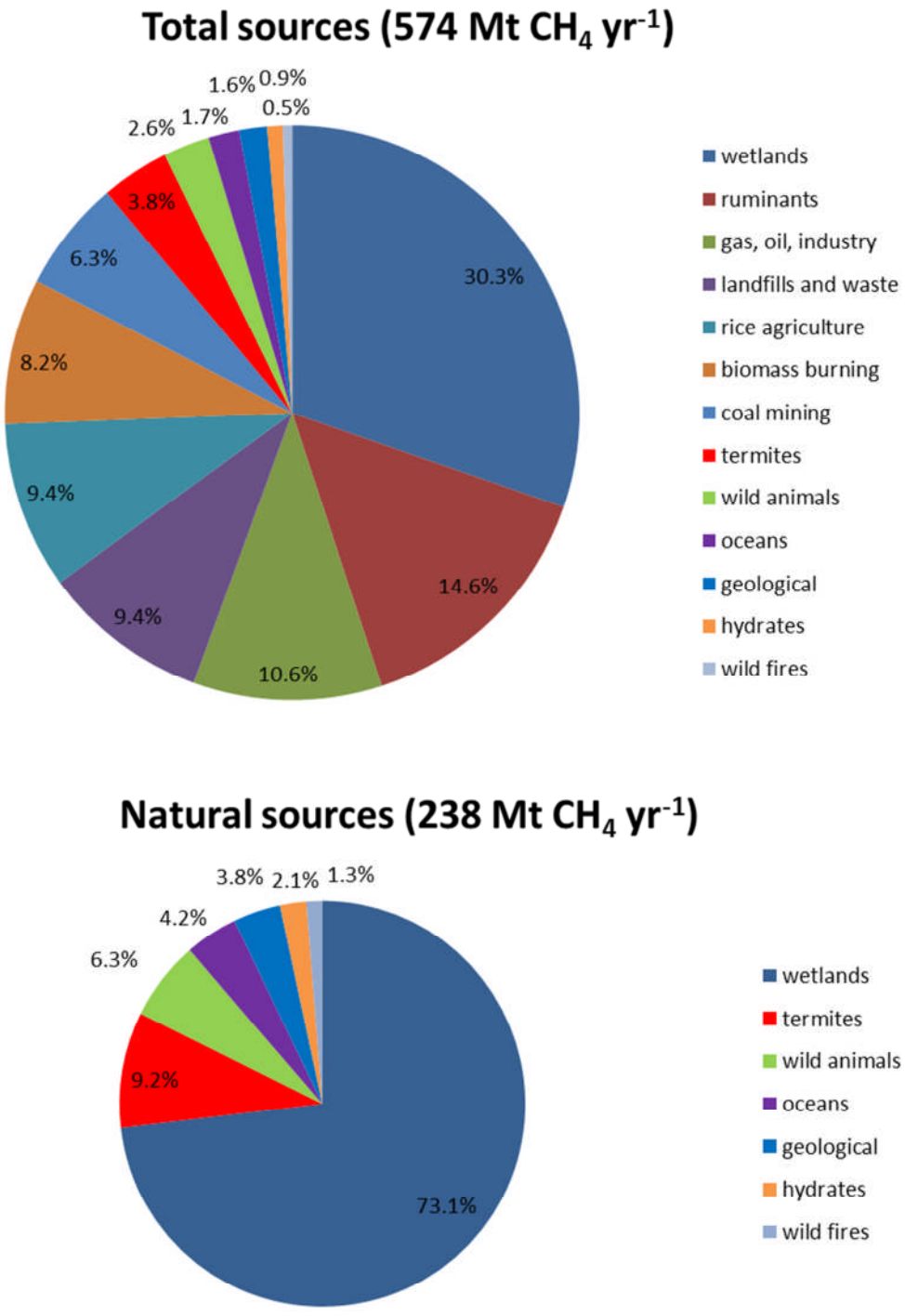

Figure 2.4: Sources of methane: total and natural (adapted from Reay et al. (2010))

In many environments CH_4 production also requires C1 compounds, which are organic compounds that do not have carbon-carbon bonds. However, it may be that in northern peatlands, predominantly those with *Sphagnum* mosses, neither C1 compounds nor acetate are utilised by methanogens for CH_4 production, which suggests that the group of methanogens responsible for H_2 oxidation and CO_2 reduction are dominant in these environments (Hines et al., 2001). However, acetate is still produced, and accrues in large concentrations, whereby the acetate then diffuses into the oxic layers of the peat and is degraded into CO_2 (Hines et al., 2001). In contrast, other studies have shown that acetate is a substrate used in CH_4 production, but it has not been ruled out that some acetate could be degraded into CO_2 (Ström et al., 2003; Ström et al., 2005). Hines et al. (2008) found that the amount of acetate produced by the anoxic decay of plant matter varied depending on the plant species; a dominance of *Sphagnum* mosses resulted in 67 % of the carbon produced through decay being acetate, compared to only 13 % in areas without any *Sphagnum* cover.

Plants deliver a range of labile carbon compounds down to anoxic peat layers through their roots. These compounds can then act as substrates, readily available for methanogenic archaea to utilise (Ström et al., 2003), alongside acetate, H_2 and CO_2 (Kotsyurbenko et al., 2004), because at the depths where methanogenesis occurs the organic matter is frequently resistant to decomposition (Ström et al., 2003). However, O_2 can also be transported down to the anoxic layer via plant roots which can hinder CH_4 production (Tuittila et al., 2000), whilst root decay can contribute to CH_4 production (Segers, 1998). Methanogens which ferment acetate are likely to be more active in the summer months when there is a greater supply of labile organic carbon (Gauci et al., 2004). Different vegetation assemblages can result in different methanogenic communities. Galand et al. (2003) showed that hummocks were populated with the Methanomicrobiales community, whereas *Eriophorum* lawns were populated with the Methanosarcinales community. Rooney-Varga et al. (2007) found that vegetation composition was the best explanatory variable the differences in methanogenic communities in two North-

American peatlands, followed by temperature. Vegetation cover can also have a further influence over CH_4 production. Lai et al. (2014) found evidence for the quick turnaround of photosynthates into CH_4 production in *Eriophorum* species with a lag of 9-12 hours. Levy et al. (2012) examined the data from multiple studies of peatland CH_4 fluxes and discovered that plant species composition was the most accurate indicator of CH_4 emissions; however, the link with vegetation cover may not be limited to CH_4 production, but could also be caused by effects on CH_4 transport or oxidation.

There are many other reported controls on CH_4 production. These include: the extent of the anoxic zone (Baird et al., 2009) which is determined by the position of the water table (MacDonald et al., 1998), as shown in Figure 2.1; the size of the methanogenic population (Segers, 1998) and the amount and quality of substrate available to them (Bergman et al., 2000); temperature and pH (Valentine et al., 1994); and the amount of rival electron acceptors present (MacDonald et al., 1998).

The quality of the substrate, as well as the quantity available to methanogenic archaea can affect CH_4 production, where quality is defined as the chemical availability of carbon for decomposition (Valentine et al., 1994). A higher quality of substrate leads to greater CH_4 production rates (Bergman et al., 2000; Granberg et al., 1997; MacDonald et al., 1998; Waddington and Day, 2007). The less decomposed the substrate is by the time it reaches the anoxic zone, the higher quality it is, which suggests that a lower water table would result in less CH_4 production (Granberg et al., 1997; Sundh et al., 1995). Methane production is exponentially linked to temperature (Dunfield et al., 1993). The Q_{10} values for CH_4 production in peatlands are generally higher than those for CO_2 production with an average value of 4.1 (Blodau, 2002). A pH of 7 is suggested as best for methanogens (Segers, 1998; Williams and Crawford, 1984); however, pH in blanket peatlands and raised bogs is acidic (Gore, 1961; Charman, 2002). Electron

acceptors are used by organisms to release energy from organic matter (Baird et al., 2009). Rival electron acceptors (for example; nitrate (NO_3^-), sulphate (SO_4^{2-}), or ferric iron (Fe^{3+})) can hinder methanogenesis (MacDonald et al., 1998; Valentine et al., 1994). In terms of electron acceptors, SO_4^{2-} is preferred over CO_2 for fermenting organic substrates and H^+ (Baird et al., 2009) because SO_4^{2-} provides more energy (Segers, 1998). Therefore, the atmospheric depositions of sulphur dioxide over peatlands from industrial incinerations that swiftly increased over the 20th century may have resulted in lowered substrate availability for methanogenic archaea (Baird et al., 2009). The substrates are instead used by sulphate-reducing bacteria which transport electrons to SO_4^{2-} in order to create hydrogen sulphide, and therefore, through a reduction in methanogenesis there is a reduction in CH_4 flux to the atmosphere (Baird et al., 2009).

2.4.2 Methane transport

Methane transport can be broken down into three sub-categories, as shown in Figure 2.1; molecular diffusion through the water and air in the soil matrix, plant-mediated transport, and ebullition (Frenzel and Rudolph, 1998).

2.4.2.1 Molecular diffusion

Molecular diffusion through peat occurs along a CH_4 concentration gradient. Diffusion is usually upwards through the peat profile towards the atmosphere. Rates of diffusion are controlled by porosity (Chanton, 2005; Tuittila et al., 2000), soil-water content (Segers, 1998) and the diffusion coefficient, which is largely dependent upon pore geometry and soil-water content (Chanton, 2005).

Although molecular diffusion has previously been thought of as the main form of CH_4 transport from peatlands to the atmosphere, it is now considered to be only one of a range of possible transport pathways (Thomas et al., 1996; Tokida et al., 2005). Molecular diffusion can occur through both the soil and through the tissue

of vascular plants (Segers, 1998). However, diffusion through the soil matrix may be the main mechanism of CH_4 escape from peatlands dominated by *Sphagnum*, which is non-vascular (Tokida et al., 2007).

2.4.2.2 Plant-mediated transport

Peatland sedges often possess a specialised vascular tissue called aerenchyma, through which O_2 is transported to the plant roots from the atmosphere (Strack et al., 2006). Gaseous transportation through aerenchyma occurs via convective throughflow, which operate via humidity-induced diffusion or thermal transpiration, and are both dependent on diffusion gradients (Armstrong et al., 1991). For example, in *Phragmites australis*, convective throughflow occurs via humidity-induced diffusion via the leaf stomata (Armstrong et al., 1991). Methane can also be transported from the rhizosphere to the atmosphere via aerenchyma (Frenzel and Rudolph, 1998). Plants growing in saturated conditions often adapt by developing spaces within their roots to store gases, known as lacunae (Thomas et al., 1996). The transport of O_2 to the plant roots occurs along a diffusion gradient opposite to that which allows CH_4 to diffuse through plants into the atmosphere (Joabsson et al., 1999). Changes in vascular plants relating to their growth and ageing, such as root porosity and surface area, may affect their transport capacities (Gauci et al., 2005).

Plants belonging to the genus *Eriophorum*, and other sedges, are classed as aerenchymous (McNamara et al., 2008). Therefore, with aerenchymous tissues and roots extending down through the peat column, sedges are well-adapted for CH_4 transport (Strack et al., 2006). *Sphagnum* mosses are commonly found on peatlands (Fechner and Hemond, 1992). However, these plants are non-vascular and do not have roots, and so cannot mediate CH_4 transport in the same way as vascular plants (Strack et al., 2006), which supports the claim that diffusion may be the main CH_4 transport pathway from *Sphagnum*-dominated peatlands (Tokida et al., 2007). Through their roots, sedges can provide labile carbon compounds to the

anoxic zone to be used in methanogenesis, thus enhancing CH_4 production. Through their ability to transport CH_4 from the anoxic zone to the atmosphere, vascular plants allow CH_4 to bypass the oxic zone within a peat soil. This by-passing effect coupled with root exudation enhancing methanogenesis may explain the results of a study which found that the CH_4 flux from vegetated peat was up to ten times greater than the CH_4 flux from bare peat (Chanton, 2005). However, Wilson et al. (2013) compared areas dominated by *Eriophorum angustifolium* against those dominated by *Juncus effusus* and *Sphagnum cuspidatum*, *Sphagnum cuspidatum* alone and bare peat, and found that the *Eriophorum*-dominated areas were the largest net carbon sinks, with bare peat areas the greatest net carbon source, which suggests that the transport of O_2 to the rhizosphere via aerenchyma may be just as important in determining the balance of CH_4 emissions as the transport of CH_4 to the atmosphere.

2.4.2.3 Ebullition

Ebullition is the release of methane from peatlands as bubbles (free-phase gas). Usually, bubbles will only form when the dissolved CH_4 and any other dissolved gases have a partial pressure greater than the peat hydrostatic pressure (Strack et al., 2005). The presence of bubbles within the anoxic zone may mean peat is not completely water-saturated even beneath the water table (Tokida et al., 2005). Before ebullition occurs, a threshold volume of bubbles may have to be reached, or if they collect in deep layers of peat the bubbles may be trapped by layers of peat above, which only infrequently allow bubbles to pass through them up to the peatland surface (Comas and Slater, 2007). Bubbles may also be released from peatlands in a constant stream (steady ebullition), but there is evidence both for and against this theory (Baird et al., 2009).

Several studies have found links between changes in atmospheric pressure and ebullition. Through laboratory-based research, Tokida et al. (2005) found that ebullition almost always occurred only during periods of falling air pressure. It was

concluded that, during times of falling atmospheric pressure, ebullition may be the main transport pathway of CH_4 from peatlands (Tokida et al., 2005). From a field study with frequent sampling rates (every six hours over five days), it was also concluded that falling atmospheric pressure led to an increase in CH_4 release via ebullition, and that ebullition is therefore an episodic process (Tokida et al., 2007). Increases in water-table depth have also been found to increase the rate of CH_4 ebullition (Baird et al., 2009), because these increases may lead to a reduction in pressure within the peat, which then causes the bubbles to expand and be released due to an increased buoyancy force (Strack et al., 2005).

Over timescales longer than the passing of an atmospheric pressure system, peat temperature and its associated effects on CH_4 production may become an important control on ebullition, because during colder periods when the peat is cooling there may be a lack of CH_4 production, leading to a lack of bubbles forming and so less ebullition (Tokida et al., 2007). Increases in temperature also cause CH_4 solubility to decrease, which may cause gas to come out of solution and add to the volume of existing bubbles (Strack et al., 2005).

The presence of bubbles within the peat may have effects on rates of molecular diffusion from peatlands because differing amounts of bubbles can change the concentration gradient along which gaseous CH_4 diffuses (Strack et al., 2005). Information on the process of ebullition and the events that contribute to its occurrence is still very much incomplete, and, because it is a process that appears to be irregular both spatially and temporally, obtaining field measurements can be problematic (Stamp et al., 2013; Tokida et al., 2005).

2.4.3 Methane consumption

Controls on CH_4 consumption include: the size of the population of methanotrophic bacteria (Segers, 1998), the position of the water table, which largely defines the

extent of the oxic zone, as shown in Figures 2.1 and 2.2 (Strack et al., 2006), the amount of water in the oxic zone (Fechner and Hemond, 1992), the amount of O_2 transported through plants from the atmosphere to the rhizosphere (Ström et al., 2005), the quantities and types of vegetation growing within the peatland (Dedysh, 2002; Strack et al., 2006), the prevailing transport pathways of CH_4 from the anoxic zone (diffusion, ebullition or plant-mediated) (Sundh et al., 1995), pH levels and temperature (Dedysh et al., 1998), and the presence of compounds that may inhibit methanotrophic activity (Dedysh, 2002; Drewer et al., 2010).

Depending on the position of the water table within a peatland there should be an oxic zone as well as an anoxic zone within the peat, and it is within this oxic zone that methanotrophic bacteria reside (Sundh et al., 1995). These bacteria may also be found below the water table within the rhizosphere of plants containing aerenchyma, as shown in Figures 2.1 and 2.2 (Le Mer and Roger, 2001). Methanotrophs are the main microorganisms to undertake CH_4 consumption in peatlands (Segers, 1998), where they convert CH_4 into CO_2 through oxidation (Le Mer and Roger, 2001). Methane is their only supplier of energy and carbon (Dedysh, 2002; Le Mer and Roger, 2001), but they also require O_2 to complete the consumption process, hence their residence in the oxic zone (Segers, 1998), and so the larger the oxic zone, the greater the potential for CH_4 consumption (Strack et al., 2006).

Methanotrophic bacteria may be most active where oxic and anoxic areas meet, such as in the rhizosphere (Frenzel and Rudolph, 1998). Oxygen is transported into the rhizosphere through plant roots via diffusion from the plant shoots (Ström et al., 2005). Therefore, CH_4 in the rhizosphere may be consumed via methanotrophs before it can enter the plant roots and be transported to the atmosphere (Ström et al., 2005). The amount of O_2 found in the rhizosphere may be dependent upon the plant species in terms of root size and ability to transport O_2 (Ström et al., 2005). Another potential reason for higher rates of methanotrophy occurring close to the

boundary of the oxic and anoxic zones is that this is the area where both of the substrates required for methanotrophy (CH_4 and O_2) are found together in the greatest abundance (Blodau, 2002).

There are two types of methanotrophy: high-affinity and low-affinity (Le Mer and Roger, 2001; Segers, 1998). Low-affinity methanotrophy occurs when CH_4 concentrations within the peat are > 40 ppm, and high-affinity oxidation occurs when CH_4 concentrations in the peat are close to atmospheric concentrations (< 12 ppm), although it is unclear which process occurs if concentrations are between 12 and 40 ppm (Le Mer and Roger, 2001). However, Segers (1998) suggested a much higher boundary between the two types of methanotrophy; 100-1000 ppm. High-affinity oxidation is thought to be responsible for the uptake of atmospheric CH_4 by soils (Bender and Conrad, 1992; Holmes et al., 1999), and is thought to account for only 10 % of all CH_4 consumption (Le Mer and Roger, 2001). Therefore, low CH_4 concentrations in the peat profile cannot occur very often, and CH_4 uptake from the atmosphere must also be a rare event (Segers, 1998). However, some studies do suggest that peatlands can be sinks of atmospheric CH_4 (Nykänen et al., 1998; Roulet et al., 1993).

The consumption of CH_4 within the oxic zones of peatlands may reduce the emissions of CH_4 produced in the peat to the atmosphere by 10-90 % (Dedysh et al., 1998), or even as much as 99 % (Ström et al., 2005). The different transport pathways of CH_4 can have an effect on consumption levels; if CH_4 diffuses into a plant through its roots it may circumvent the oxic zone within the peat and so may not be consumed. Frenzel and Rudolph (1998) concluded that methanotrophic activity only occurred in *Eriophorum* plants at very low rates, which suggests that methanotrophs do not reside within vascular plant tissues, unlike in *Sphagnum* plants where methanotrophs have been shown to reside in the hyaline cells of the plant (Raghoebarsing et al., 2005). If CH_4 is transported into the oxic zone via molecular diffusion through the peat it has a much greater chance of being

oxidised than if it is transported via ebullition, because the bubbles can pass through the oxic zone much quicker making them less available for consumption (Rosenberry et al., 2006; Sundh et al., 1995).

Oxygen content within the soil has been cited as the main limiting factor of methanotrophic activity (Le Mer and Roger, 2001); however, there are also claims that methanotrophs can endure oxygen levels as low as 0.1 mg L^{-1} (McDonald et al., 1996), and may even be able to function in anoxic environments (Sundh et al., 1995). In daylight conditions, higher O_2 concentrations on the peat surface, as a result of photosynthesis, could lead to higher rates of oxidation (Nedwell and Watson, 1995; Thomas et al., 1996). Another factor affecting methanotrophy is pH levels. Methanotrophs may be unable to grow below pH levels of 5.0 (Hanson and Hanson, 1996). However, pore water in *Sphagnum* bogs has pH levels of 3.5–5.0, and methanotrophy has been observed in such systems (Dedysh, 2002; Dunfield et al., 1993; van Winden et al., 2012).

Another factor influencing methanotrophy is temperature, with methanotrophic rates increasing with temperature (Dedysh et al., 1998). However, methanotrophy may have a weaker relationship with temperature than methanogenesis (Tuittila et al., 2000). Indeed, the average Q_{10} value for CH_4 consumption (1.9) is smaller than for CH_4 production (4.1) (Blodau, 2002). The position of the water table may have an effect on soil temperature and therefore CH_4 oxidation rates. With a water table close to the ground surface there is an established connection between CH_4 emissions and temperature (Tuittila et al., 2000). However, with a low water-table position soil temperature may have very little effect on CH_4 emissions (Nykänen et al., 1998). The amount of water present in the oxic zone may also have an influence on methanotrophy; CH_4 oxidation rates may rise with a reduction in water content because of an increase in CH_4 transport to methanotrophs due to the increase in air-filled porosity (Fechner and Hemond, 1992). Inputs of nitrogen may affect oxidation rates (Drewer et al., 2010); however methanotrophs may be

able to adapt to differing amounts of nitrogen within their environment (Dedysh, 2002).

2.4.4 Methane consumption and *Sphagnum* mosses

Methane fluxes from peatlands dominated by *Sphagnum* species are often lower than from peatlands dominated by other species, particularly vascular plants (McNamara et al., 2008; van Winden et al., 2012). Reasons for this difference in CH_4 fluxes are often attributed to the substrate supply that vascular plants can provide via their roots to methanogens, and the transport pathway that exists from the anoxic zone and through the aerenchymous tissue of vascular plants, bypassing the oxic zone (Joabsson et al., 1999). However, a symbiotic relationship between methanotrophs and *Sphagnum* mosses has been demonstrated in some studies, which may be another reason for the difference in CH_4 fluxes (Kip et al., 2010; Putkinen et al., 2012; Raghoebarsing et al., 2005). This 'symbiotic' relationship is described by the authors above as where the methanotrophs provide CO_2 for the Sphagnum mosses to use for photosynthesis, and the O_2 produced during photosynthesis can be used by methanotrophs to complete the methanotrophic process (Kip et al., 2010; Putkinen et al., 2012; Raghoebarsing et al., 2005). It is recognised that the relationship described above is not a symbiosis in the true meaning of the word; it is not that neither Sphagnum mosses nor methanotrophs can survive without the other. Therefore, this relationship is deemed to be more accurately described as mutually beneficial.

Sphagnum mosses contain chlorophyllose cells, which perform the photosynthetic functions, and are surrounded by larger hyaline cells, which are dead and often filled with water (Rinnan and Holopainen, 2004; Rydin and Jeglum, 2013). In *Sphagnum*-dominated peatlands CH_4 oxidation can occur at high rates, and one of the reasons for this is because methanotrophs can reside within the hyaline cells and on the stems of *Sphagnum* mosses (Raghoebarsing et al., 2005). Kip et al. (2010), Larmola et al. (2010) and Raghoebarsing et al. (2005) found that 10-35 % of

the carbon found in *Sphagnum* mosses studied originated from CH_4 oxidation. Several studies have found this mutually-beneficial relationship to be strongest when the *Sphagnum* mosses are submerged (Basiliko et al., 2004; Kip et al., 2010; Raghoebarsing et al., 2005). The diffusion of CO_2 and O_2 is much slower through water than through the air (Haynes, 2012), which could retard photosynthesis and methanotrophy in a submerged environment; although, the O_2 from photosynthesis and CO_2 from methanotrophy help to bypass this issue. However, Putkinen et al. (2012) found that methanotrophs can survive transportation through water, which suggests that although there is a mutual benefit to each party as described above, methanotrophs are not solely dependent on a habitat within *Sphagnum* mosses to survive.

During restoration, it may not always be possible for land managers to keep the water table of a peatland close to the surface, and so *Sphagnum* may experience drought. Drought can cause damage to the photosynthetic abilities of *Sphagnum* mosses (Demmig-Adams and Adams, 1992; Harris, 2008), and repeated cycles of drought may permanently damage these photosynthetic functions (Schipperges and Rydin, 1998). However, no literature has yet been found as to whether the hyaline cells, are affected by drought, and if so, what effect this may have on the mutually beneficial relationship between methanotrophy and *Sphagnum* mosses. As the supply of O_2 from photosynthesis is no longer available for the methanotrophs to aid their consumption of CH_4, there should be reduced levels of methanotrophy. If *Sphagnum* mosses are subjected to drought, it is also unclear what would happen in terms of methanotrophy if the *Sphagnum* mosses were once again submerged. If the mutually-beneficial relationship during submergence reported in the literature existed prior to drought, it is unclear if it would be re-established if the *Sphagnum* mosses were once again submerged. Further rationale for these research gaps will be provided in Chapter 6.

2.5 Diurnal variation in gaseous fluxes

The field measurements for many studies that examine gaseous fluxes from peatlands are only conducted during daylight hours. To obtain measurements of NEE, CO_2 fluxes are often measured twice using a chamber; once without a shroud to allow light to penetrate into the chamber for NEE, and once with a shroud to block the light and simulate night conditions for ecosystem respiration. However, temperature does not change to night-time conditions for these measurements, which could mean the results do not reflect true night-time flux values. The controls governing CO_2 fluxes from peatlands are well-established; PAR and temperature (Hendriks et al., 2007; Shurpali et al., 1995; Yu et al., 2013). However, if night-time conditions are not being accurately simulated, the data upon which any CO_2 NEE modelling is based could be inaccurate. Many authors have reported on a link between photosynthesis and ecosystem respiration (Clay et al., 2012; Larsen et al., 2007; Lasslop et al., 2010; Migliavacca et al., 2011). Larsen et al. (2007) found a significant relationship between photosynthesis and ecosystem respiration through an incorporation of a photosynthesis function into an ecosystem respiration model. The vegetation type studied was *Calluna vulgaris*, and the study suggested that ecosystem respiration was largely influenced by the most recently sequestered carbon of the plant (Larsen et al., 2007). Therefore, if a dark chamber test occurs during daylight hours, the ecosystem respiration results obtained could be greatly different to a test that occurred in the middle of the night, when photosynthesis had not occurred for several hours. Dixon (2012) indicated that an exclusion of photosynthesis in any models of ecosystem respiration could place undue importance on temperature as a predictive variable of ecosystem respiration rates. Therefore, night-time measurements of CO_2 flux will provide an insight as to whether daytime measurements of ecosystem respiration to also accurately represent night-time ecosystem respiration.

It is not yet well established if CH_4 fluxes follow a diurnal pattern, because most of the studies already conducted have not been replicated on the same vegetation

compositions, and have found different variations (Long et al., 2010; Mikkelä et al., 1995; Wang and Han, 2005; Yavitt et al., 1990). As with CO_2 fluxes, CH_4 fluxes are often only measured during the daytime, and are used to represent emissions for a whole day; often longer if seasonal or annual flux calculations are needed (Coulthard et al., 2009). If CH_4 emissions do show a significant diurnal pattern, daytime-only measurements could be an over- or underestimation of the emissions, which will impact on any projections that these fluxes are used to estimate. Further rationale for these research gaps will be provided in Chapter 5.

2.6 Summary of research gaps

An accurate understanding of the gaseous flux response to peatland restoration is important in terms of the enhanced greenhouse effect. Atmospheric levels of both CO_2 and CH_4 are rising, causing the Earth's climate to warm which has associated negative effects such as rising sea levels and increased risk of flooding. Therefore, a greater knowledge of natural sources of these gases so that they can be mitigated is important. There are relatively few studies that have examined the effects of peatland restoration on gaseous fluxes over long periods of time; longer than seven-10 years. However, peatland management strategies usually cover much longer time periods (20-40 years). Therefore, assumptions must be made as to the response of restored peatlands in terms of gaseous fluxes over longer timescales. Some researchers have made the assumption, based on limited data, that in the long-term, the GWP of restored peatlands will decline and possibly even become negative (net cooling effect) (Bain et al., 2011; Joosten et al., 2006). Therefore, an increased understanding of how gaseous fluxes from peatlands change with time following restoration, particularly over timescales in excess of 10 years, is important for peatland management and climate change predictions. Research questions 1 and 2 address this issue:

1. **Do CH_4 and CO_2 emissions from peatlands change with time following restoration?**

2. **What are the main drivers of CH_4 and CO_2 emissions in restored peatlands?**

Measurements of CH_4 and CO_2 fluxes often only occur during the daytime, depending on the monitoring equipment available. Diurnal variations of CO_2 fluxes are well-understood, due to the strong influence of PAR and temperature (Shurpali et al., 1995; Yu et al., 2013). However, although light can be blocked out easily during measurements by the use of a shroud to simulate night-time conditions during ecosystem respiration measurements, temperatures cannot be altered so easily. Therefore, ecosystem respiration measurements taken during the daytime could be under- or overestimations, and so a greater understanding of actual night-time CO_2 fluxes is needed. The diurnal variations in CH_4 fluxes are not as well understood; previous studies have found different patterns depending on the time of year, the growth stage of the vegetation, and the vegetation composition (Bäckstrand et al., 2008; Kim et al., 1998b; Long et al., 2010; Mikkelä et al., 1995). Also, very few studies have been conducted in areas with similar vegetation compositions, and so it is unknown if CH_4 fluxes from peatlands with similar vegetation compositions will have the same diurnal responses. Therefore, CH_4 flux measurements taken during the daytime could be over- or underestimations, which would have consequences for any scaling-up calculations to seasonal or annual flux totals, and subsequent consequences on GWP calculations. Research questions 3 and 4 address this issue:

3. **Do CH_4 emissions vary diurnally, and if so, what are the main drivers of the diurnal variations?**
4. **Does the diurnal variation in CO_2 emissions result in positive or negative net ecosystem exchange (NEE)?**

Peatlands dominated by *Sphagnum* mosses often have lower CH_4 emissions than areas with other dominant vegetation types (McNamara et al., 2008; van Winden

et al., 2012). One reason cited for these lower CH_4 fluxes is the presence of methanotrophs, which have displayed a preference for residing within the cells of *Sphagnum* mosses (Raghoebarsing et al., 2005). Some authors have defined the benefits that *Sphagnum* mosses and methanotrophs can provide for each other as a symbiosis; a relationship that is even more prominent when the *Sphagnum* mosses are submerged (Basiliko et al., 2004; Kip et al., 2010). Through photosynthesis, the *Sphagnum* mosses can provide O_2 for the methanotrophs to oxidise CH_4 into CO_2, and so the CO_2 is available for the *Sphagnum* mosses for photosynthesis (Putkinen et al., 2012). Drought can damage the photosynthetic abilities of *Sphagnum* mosses (Harris, 2008); however, it is unclear if drought has any effects on the abilities of methanotrophs to function. A main goal of peatland restoration is to maintain the WTP near the peat surface; however, this goal is not always possible to maintain all of the time, and so *Sphagnum* mosses on a restored peatland can experience drought, and then re-submergence. It is also unclear if the submergence after drought will affect the relationship between methanotrophs and *Sphagnum* mosses, if it was present originally. Research questions 5 and 6 address this issue:

5. **Does drought affect methanotrophic activity within *Sphagnum* mosses?**
6. **Does submergence affect methanotrophic activity within *Sphagnum* mosses that have been subjected to drought?**

Chapter 3: Field methods and analysis of field samples

3.1 Study area

3.1.1 Location

This study was conducted on Thorne and Hatfield Moors, South Yorkshire (53.6 N -0.91 W and 53.5 N -0.93 W respectively), which together comprise the only remnants of the largest lowland raised bog complex in the UK covering 28.87 km^2, as shown in Figure 3.1 (Cris et al., 2011). The sites now form the Humberhead Peatlands National Nature Reserve, which is part of the Humberhead Levels. The Humberhead Levels lie on the borders of Yorkshire, Lincolnshire and Nottinghamshire, between the Rivers Ouse and Trent before their confluence at the Humber Estuary.

Figure 3.1: Location of Thorne and Hatfield Moors within the UK, with nearby watercourses.

Thorne and Hatfield Moors provided an ideal location for this study, because peatland restoration through rewetting occurred across the both Moors in stages (1997, 2003-5 and 2008). These sub-sections of different restoration ages provided a space-for-time substitution that allowed for the effects of peatland restoration on gaseous fluxes to be examined over three time periods: 15, 9 and 4 years.

3.1.2 Brief history

The Humberhead Levels wetland area formed at around 11,000 BP, with peat formation starting at 3,000-5,200 BP (Caufield and Godwin, 1991). The areas now known as Thorne and Hatfield Moors were part of this large wetland area. The underlying geology of the area is comprised of Sherwood Sandstone with an overlying layer of lacustrine clay deposited by the post-glacial Lake Humber (T. Kohler, pers. comm.). There are sand lenses in place over Thorne and Hatfield Moors, which provide a direct connection to the underlying geology; however, the sites are mostly considered to have perched water tables (T. Kohler, pers. comm.).

There is evidence of peat extraction in the area dating back to the 14th century (T. Kohler, pers. comm.); however the first major anthropogenic modification was in the 17th century when drainage began (Caufield and Godwin, 1991). The reason for drainage was to make the land more suitable for hunting (Caufield and Godwin, 1991), followed by wet-warping (controlled flooding to deposit silt) to improve the land for agriculture in the late 18th and early 19th centuries (Eversham, 1991; Smart et al., 1986). Peat extraction was also occurring during this time period (Bonn et al., 2009), but on a smaller scale than in later years. In the late 19th century a network of ditches approximately 22.5 km long was dug into the southern half of Thorne Moors to both drain the peat and aid peat removal from the site through the use of horse-drawn barges (Eversham, 1991; Limbert, 1986; Smart et al., 1989). The most recent disturbance to Thorne and Hatfield Moors was peat extraction via milling, which started in the mid-1980s and continued until 1992-2004. This method of peat extraction only occurred on the northern half of Thorne Moors,

and on 80 % of Hatfield Moor. Milling involves skimming 4-6 cm of peat from a previously deep-drained area every 3-6 weeks (Eversham, 1991; Bonn et al., 2009). To drain the peatlands in preparation for milling, 35.4 km of new drainage ditches were dug, vastly increasing the size of the drainage system already in place (Caufield and Godwin, 1991).

Natural England have managed Thorne and Hatfield Moors since 1992 (Bull, 2003), and an agreement with the peat cutters was signed in 1994 (T. Kohler, pers. comm.). Initially, Natural England managed a small area of Thorne Moors until extraction ceased in 2004, when they took over complete management of the two sites. As milling resulted in all of the vegetation being stripped from the peat, their starting point for restoration work was a bare peat surface, with the remaining peat depth varying across the site from only approximately 30 cm to > 1 m. The main aim of restoration for Natural England was for biodiversity, and the sites have Special Area of Conservation and Special Protection Area status (T. Kohler, pers. comm.). This thesis will examine the effects of restoration on the gaseous carbon balance of the sites, which will provide an insight as to whether restoration can improve biodiversity and the gaseous carbon balance simultaneously. Restoration via rewetting began with the construction of peat bunds to create compartments of 0.02-0.03 km^2 to aid water-level management. Raising the water table encourages the reestablishment of growth of peat-forming bog species, mainly comprising *Sphagnum* mosses and cotton grasses.

3.1.3 Specific site locations

Four sites within Thorne and Hatfield Moors were monitored for gaseous fluxes over a 13 month period. Table 3.1 provides more information on the sites. To ensure that conditions under which microbial processes relating to gas exchange could occur were as similar as possible, peat depth was similar at all sites. Vegetation coverage was not uniform, as vegetation type could be a factor of time since restoration started, relating to successional processes. A control site was also

chosen, where restoration had so far not been achieved due to the layout of the drainage channels in this area of the site. Therefore, conditions at the control site were very similar to those when milling occurred; the peat surface was devoid of any vegetation and the water table several decimetres below the peat surface. However, the peat depth was similar to that at the other three sites (Table 3.1). Figure 3.2 shows photographs of each of the four study sites.

Table 3.1: Information about each study site

Year restoration started	Site ID	National grid reference	Peat depth (cm)	Dominant vegetation type	Mineral substrate
1997	A	SE 72163 16667	45-60	*Eriophorum angustifolium* and *Eriophorum vaginatum*	Clay and sandy clay
2003	B	SE 71617 17205	45-80	*E. angustifolium* and *E. vaginatum*	Clay and sandy clay
2008	D	SE 72794 05753	50-85	*Sphagnum cuspidatum*	Sand
Control	C	SE 72025 18440	35-60	None	Sand

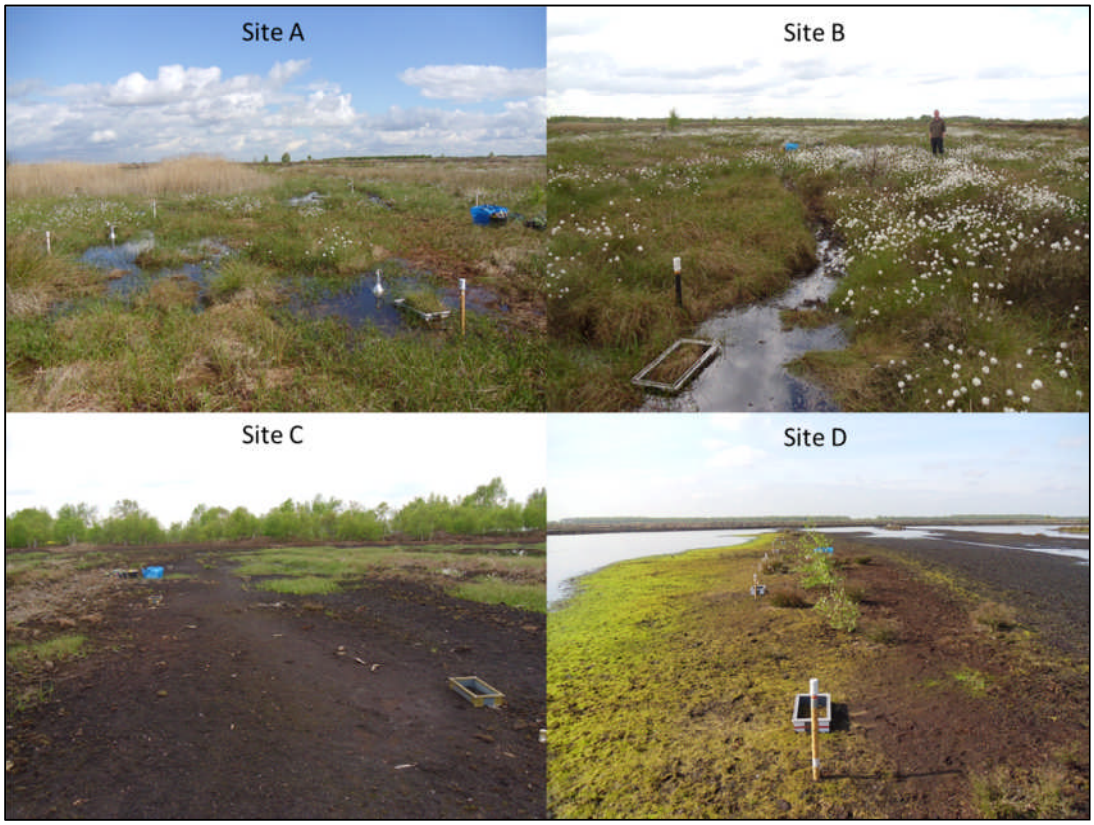

Figure 3.2: Photographs of each of the four study sites (Photographs taken on 08/05/2012 for Sites A and B, and on 09/05/2012 for Sites C and D)

3.1.4 Climate

From data collected at Thorne Moors by Natural England, with supplementary data from the UK Met Office website, the average annual rainfall for this area was 612 mm between 1992 and 2010, with a minimum annual total of 479 mm in 1996 and a maximum annual total of 850 mm in 2000. In the three years leading up to this study, the total annual rainfall for each year was less than the long-term average, with 584 mm in 2009, 572 mm in 2010 and 507 mm in 2011. Therefore, when this study started in September 2011, conditions on Thorne and Hatfield Moors were very dry with a low water-table position. However, 2012, the year that the majority of this field study occurred, was wetter than average with an annual total of 852 mm, making it the wettest year on record between 1992-2012.

Thorne and Hatfield Moors lie within the E/NE region of England, as defined by the Met Office to extend from the Northumbrian-Scottish border to the Lincolnshire-East Anglian border (Met Office, 2013). The mean annual temperature from 1910 to 2012 was 8.6 °C (Met Office, 2013). An automatic weather station (AWS, more detail provided in Section 3.2.3.2) deployed at Thorne Moors recorded a mean temperature of 9.6 °C for 2012 (only until 05:00 28/11/2012). The Met Office data for 2012 for the E/NE region was 8.8 °C.

3.2 Field and laboratory methods

3.2.1 Overview

In order to address research questions 1 and 2, fluxes of CH_4 and CO_2 needed to be determined at each of the four study sites over a one-year period to examine both seasonal and annual fluxes and identify any changes in fluxes both within and between sites. Measurements of environmental variables shown in the literature to influence these gaseous fluxes were also needed to address research question 2.

Gaseous fluxes of CH_4 and CO_2 were determined using static closed chambers at each of the four study sites, as detailed and shown in Table 3.1 and Figure 3.2. Six collars were installed at each site, encompassing the dominant vegetation of the site to ensure that the fluxes measured would be representative of the wider restoration compartment. Section 3.2.2 provides detailed information on the methods available and chosen for measuring gaseous fluxes.

Fieldwork was conducted over 13 months at Thorne and Hatfield Moors between 29/09/2011 and 25/10/2012. During the winter months (November-March) fieldwork was conducted monthly, and during the summer months (April-October) fieldwork was conducted fortnightly. This time period was chosen in order to be able to calculate annual fluxes that included winter fluxes, and the frequency of

sampling increased during summer months due to an expected rise in microbial activity with the warmer temperatures. Each sampling visit involved the following

- Photographing each collar to record any vegetation change
- Measuring soil temperature in the centre of each collar
- Measuring water table position at each collar
- Flux chamber tests for CH_4 and CO_2
- Downloading data from AWS

Collar photographs and soil temperature measurements were taken shortly after arrival to the sites on each visit. The timings of chamber tests for CH_4 sampling and CO_2 measurements were varied as much as possible between different field visits, both within and across sites in order to minimise any diurnal bias in the test times.

Collar locations were determined based on the dominant vegetation type within the particular compartment. If more than one vegetation type was deemed to be dominant, then collars were distributed equally over both vegetation types. Each collar was located at least two metres away from any adjacent collar. Table 3.2 shows the dominant and other vegetation types within each collar, as identified from photographs taken in October 2011, July/August 2012 and October 2012.

Table 3.2: Vegetation present within each collar. Site C is excluded due to the lack of vegetation.

Collar	Dominant vegetation	Other vegetation
A1	*E. vaginatum*	None
A2	*E. angustifolium*	*Polytrichum commune*
A3	*E. angustifolium*	None
A4	*E. vaginatum* and *E. angustifolium*	None
A5	*E. angustifolium*	None
A6	*E. angustifolium*	*S. cuspidatum*
B1	*E. angustifolium*	None
B2	*E. angustifolium*	None
B3	*E. angustifolium*	*E. vaginatum* and *S. cuspidatum*
B4	*E. vaginatum*	*E. angustifolium*
B5	*E. vaginatum* and *E. angustifolium*	None
B6	*E. vaginatum* and *E. angustifolium*	None
D1	*S. cuspidatum*	None
D2	*S. cuspidatum*	None
D3	*S. cuspidatum*	*E. vaginatum* and *Calluna vulgaris*
D4	*S. cuspidatum* and *C. vulgaris*	None
D5	*S. cuspidatum*	*C. vulgaris*
D6	*S. cuspidatum*	*C. vulgaris*

Six collars and six dipwells were installed at each site in August 2011, with each collar having an adjacent dipwell to form a plot. Installation occurred approximately six weeks before field measurements commenced in order to allow the system to recover from the disturbance caused by installation. However, in mid-September 2011 the collars and dipwells installed at Site C were vandalised, and so were removed for repair and reinstalled on September 28th 2011, only one day before field measurements commenced. Site conditions in August and

September 2011 were very dry, with the water table position at least 20 cm below the peat surface on each of the four study sites. Due to the very dry conditions, full boardwalks were not deemed to be necessary at the start of the monitoring; however, small pieces of boardwalk were used at each site to place beside each collar during chamber measurements to reduce any observer disturbance.

3.2.2 Gaseous flux measurements

3.2.2.1 Available methods

The two main methods for measuring gaseous emissions from soils involve using either flux towers or flux chambers (Baird et al., 2009). The most common type of flux tower method is eddy covariance, which operates on the landscape scale (10 m^2 and upwards), whereas flux chambers are used on smaller scales (usually < 1 m^2) (Baird et al., 2009; Schrier-Uijl et al., 2010).

Eddy covariance measurements assume that gaseous concentrations are uniform horizontally, and only vary vertically (Schrier-Uijl et al., 2010). Gaseous concentrations are measured with sensors within the tower, along with temperature and wind speed (Schrier-Uijl et al., 2010; Denmead, 2008). One advantage of this method, in comparison with flux chambers, is that it can run continuously (Schrier-Uijl et al., 2010). However, given the landscape-scale coverage this method provides, and the assumption that there is no horizontal variation in fluxes, it may not be reliable where the landscape topography or vegetation is not homogenous (Baird et al., 2009). For CO_2 fluxes, eddy covariance can only measure NEE, but many methods exist to partition the data into the components of gross photosynthesis and ecosystem respiration (Desai et al., 2008; Reichstein et al., 2005). Of all the data that an eddy covariance system collects, large quantities can often be lost to system faults: 20 % (Rinne et al., 2007) 55 % (Jackowicz-Korczyński et al., 2010), 74 % (Wille et al., 2008). However, given that eddy covariance enables continuous monitoring, the amount of data left may still be comparable to, if not far-exceeding the amount of data that could be collected

'by hand' on a monthly or fortnightly scale. Once all faulty data had been removed, Rinne et al. (2007) were left with 6266 CH_4 flux measurements from half-hourly recordings. There are also many gap-filling methods available for when data is lost through system faults or quality control measures (Moffat et al., 2007). Methane flux measurement by eddy covariance is not as widespread compared with CO_2 flux measurement because of the difficulties in accurately measuring CH_4 concentrations due to their low field concentrations (Hendriks et al., 2008). However, there are many new techniques that have been trialled in recent years to enhance CH_4 flux measurements through eddy covariance (Baldocchi et al., 2012; Detto et al., 2011; Herbst et al., 2013; McDermitt et al., 2011).

Flux chambers allow the user to measure gaseous fluxes on a smaller scale than towers and are cheap to construct and use. There are three main types of chamber: flow-through, dynamic-closed and static-closed (Denmead, 2008). The basic principle of the latter two is as follows. A chamber is placed on the peatland surface. If a gas, such as CH_4, is being emitted from the peatland its concentration in the chamber will increase over time. By measuring the gaseous concentration over time, it is possible to estimate flux. Due to the small surface area covered by a chamber system in comparison to the eddy covariance method, replicates are needed (Denmead, 2008). However, there can be very large uncertainties associated with fluxes measured from chambers when it comes to up-scaling the results to a wider scale, which can be problematic when predicting the responses of gaseous fluxes to changes in land management or climate (Dinsmore et al., 2009b; Olson et al., 2013).

To work effectively, a chamber must be sealed at its contact with the soil surface. One method of sealing the chamber is to use a collar, inserted into the peat to 5-20 cm depth (Baird et al., 2009). The flux chamber can then be fitted to the collar with a gas-tight seal when needed (Baird et al., 2009). One of the most common methods to create a seal reported in the literature is the use of a gutter fitted to

the top of the collar. When a measurement is required, the gutter is filled with water and the base of the chamber placed in the gutter (Blodau et al., 2007; Bubier et al., 2005; Nykänen et al., 1998; Schrier-Uijl et al., 2010). However, other methods to create a gas-tight seal between collar and chamber include a polypropylene flange (Drewer et al., 2010) and silicone tubing attached to the chamber base (Juszczak and Augustin, 2013). A drawback of this method, in comparison to eddy covariance is the amount of disturbance caused to the peat through the insertion of multiple collars. Further disturbance can then be caused by the operator repeatedly visiting each collar during the sampling time period. Disturbance can be reduced through the use of boardwalks or snow shoes; however, the use of these techniques are unlikely to remove all disturbance.

As noted above, three types of flux chamber may be used. Flow-through chambers operate by having a constant flow-through of outside air. The concentrations of this air are measured at the entry point to the chamber and at the exit point, and the change in concentration, and therefore the flux relating to the area of soil between the two points can be calculated using:

$$\boldsymbol{F_g = v(\rho_{g,o} - \rho_{g,i})/A} \qquad \textbf{Equation 3.1}$$

where F_g is the flux density of gas at the surface (kg m^{-2} s^{-1}), v is the volume flow rate (m^3 s^{-1}), $\rho_{g,o}$ is the gas concentration of the air leaving the chamber (kg m^{-3}), $\rho_{g,i}$ is the gas concentration of the air entering the chamber, and A is the surface area the chamber covers (m^2) (Denmead, 2008). The advantage of flow-through chambers is that they reduce the risk of too large a concentration building up inside the chamber, which prevents further diffusive transport of gas from beneath the peat into the chamber (Denmead, 2008). However, small changes in gaseous concentrations within this type of chamber may be missed (Denmead, 2008).

Dynamic-closed chambers and static closed chambers do not have a constant flow-through of air, but allow gaseous concentrations to build in the chamber with time. Dynamic-closed chambers are linked to a gas analyser, with gas circulated in a loop between the chamber and the analyser. Some dynamic-closed chambers can be designed to close and open automatically, requiring less manual work (Denmead, 2008). However, many gas analysers cannot be used in rainy conditions due to the risk of water damaging the internal dynamics of the instruments; therefore, their use can be very limited depending on the conditions encountered in the field, which causes further uncertainty when attempting to model and results on a temporal scale. Static-closed chambers operate by the user taking gas samples from the chamber via a syringe at regular time intervals during the measurement period. These samples can then be analysed in the laboratory for their concentrations (Denmead, 2008). Fluxes from closed chambers are calculated using:

$$\boldsymbol{F_g = (V/A)d\rho_g/dt} \qquad \textbf{Equation 3.2}$$

where V (m^3) is the chamber headspace volume and t (s) is time and all other components are as in Equation 1 (Denmead, 2008).

The aim of this study was to assess the potential differences in gaseous fluxes between different areas of Thorne and Hatfield Moors, and so for eddy covariance to be a useful method of flux measurement, multiple towers would be needed. Therefore, despite the larger amount of data that could have been collected, this method would have been too expensive given the funds available for this project and other necessary expenditures. Flux chambers were chosen for this study due to their low cost, easy assembly and the ability to contain from specific vegetation types within a collar. Due to cost, ease of construction and ease of use in the field, PVC collars with gutters were chosen. For CH_4 flux measurements, static-closed

chambers were used and for CO_2 flux measurements the same chambers were converted to dynamic-closed chambers through the attachment of a gas analyser; however, they were still operated manually.

3.2.2.2 Flux chambers and collar design and installation

Figures 3.3 and 3.4 show the chamber and collar set-ups for CH_4 sampling and CO_2 flux measurements respectively. Following the design of Stamp (2011), chambers were constructed from acrylic plastic of 6 mm width, with dimensions of 46.5 x 26.2 x 26 cm, purchased from Aquatics Online. Four holes were drilled into the top of each chamber. Thin acrylic plastic tubes (8 mm ID) were fitted through two of the holes and sealed in place with aquarium-grade silicone sealant (Silver Label). An uninflated balloon was fitted over the inside end of one tube to allow for pressure equilibration during chamber tests. A rubber septum (Suba Seal, Sigma Aldrich) was fitted over the outside end of the other tube to allow for gas samples to be taken via syringe. The third hole was for a rubber bung, through which a Commeter C4141 thermo-hygro-barometer probe (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 to measure chamber conditions during sampling. The fourth hole was for another rubber bung, through which the intake and outflow tubes of an infra-red gas analyser (IRGA) (EGM-4, PP Systems, Hitchin, UK) (accuracy: < 1 % of span concentration) for CO_2 measurements (parts per million (ppm)) were fitted into the chamber. When CH_4 samples were being taken, this hole was blocked using a solid rubber bung. Gas-tight seals were created around all bungs using petroleum jelly. A small handheld, battery-operated fan was fixed to one of the longer walls inside each chamber, in order to mix the air within the chamber headspace and ensure that the gases within were equally mixed. If gases were not equally mixed, there would be a risk of sampling air from concentrated pockets of unmixed gas, which could give misleading results. To prevent artificial warming in the chamber for CH_4 sampling and light penetration into the chamber for CO_2 measurements in dark conditions, removable shrouds made from reflective

radiator backing were used. Unfortunately, the radiator backing could not completely prevent chamber heating during days of strong sunlight; however, the fan inside the chamber assisted in mixing the chamber air to encourage an even temperature throughout the chamber. Heating of the gas within the chamber during the flux test would expand in volume according to Charles's Law. An increased volume of gas, caused only by a rise in temperature and not by increased concentrations diffusing into the chamber from the peat, could lead to an overestimation of the calculated CH_4 fluxes, especially on days with strong sunlight. Baird et al. (2009) indicated that this problem could be reduced by installing a heat exchanger within the chamber; however, this addition was not possible for this study.

Collars were constructed from sheets of polyvinyl chloride (PVC) (47.2 x 22.3 x 15 cm), held together at the corners using plastic angle made from un-plasticised PVC (UPVC) and held together with aquarium-grade silicone sealant. Gutters for the collars were made from cable trunking (2.5 x 1.6 cm) and were fixed to the top of each collar using silicone sealant. During chamber tests, the gutters were filled with water, and the chambers placed inside the collar. This created a gas-tight seal, sealing off the chamber headspace from the surrounding atmosphere to allow for gas concentrations to accumulate for sampling. Water levels in the gutters were regularly checked and maintained during chamber tests. For use on areas with tall vegetation, extension collars were also constructed and can be seen in Figures 3.3 and 3.4. The extension collars were constructed from the same materials and to the same dimensions as described above. When required, an extension collar was placed into the water-filled gutter of the collar in the peat, and the chamber was placed into the water-filled gutter of the extension collar. For installation, collars were placed on the peat surface, and if vegetation was present any leaves or plants that were trapped under the base of the collar were freed and placed on the correct side of collar depending on their origin. Scissors were used to cut around the base of the collar, down into the peat, and the collars were pushed down into place. Where tough roots were encountered that the scissors

could not break through, a bread knife was used. Each collar was inserted to approximately 8 cm depth, and no plant dieback was observed following installation. Due to the use of a water-filled gutter, the collars had to be made level during installation, and were regularly checked to ensure they were still level throughout the fieldwork period.

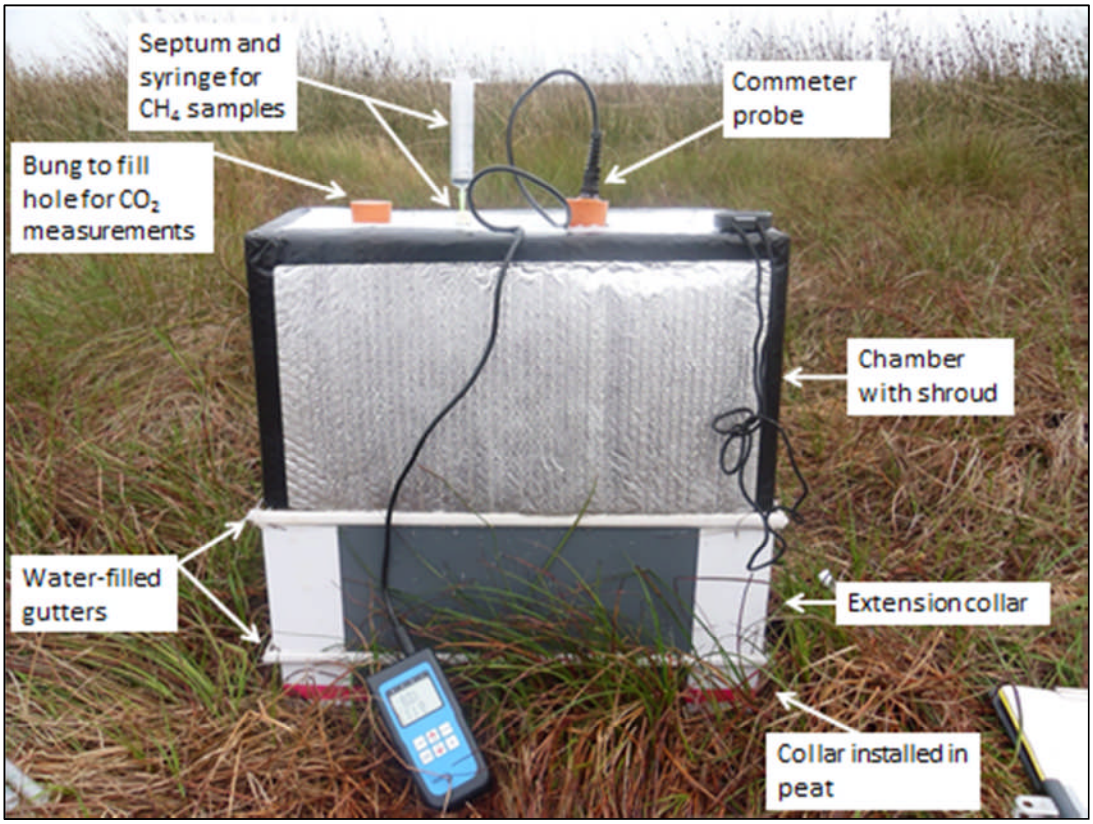

Figure 3.3: Labelled picture of chamber setup for CH_4 sampling

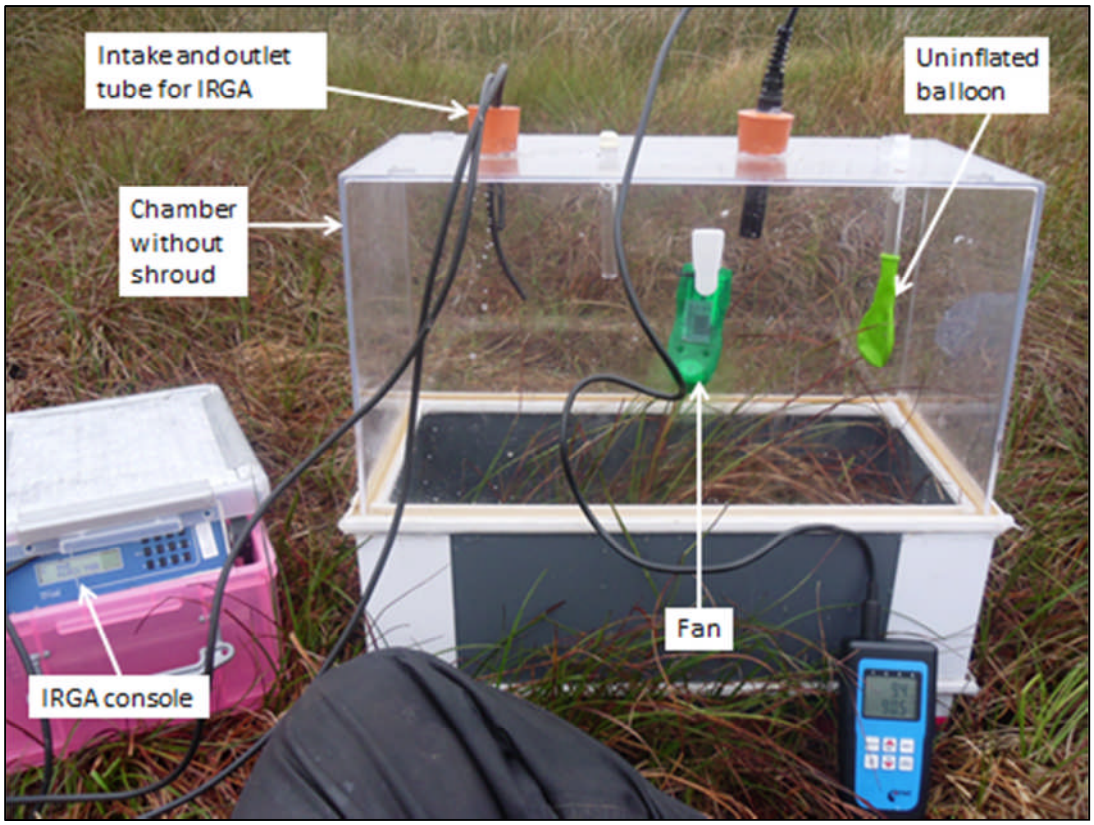

Figure 3.4: Labelled picture of chamber setup for CO_2 measurements

3.2.2.3 Chamber sampling

For CH_4 sampling, the chamber, as shown in Figure 3.3 was placed into the water-filled gutter of the collar. Immediately after closure, the first sample of gas was extracted via a syringe fitted with a hypodermic needle through the septum at the top of the chamber. The 14 ml gas sample was placed into a 12 ml pre-evacuated exetainer (Labco Limited, Lampeter, UK), and the purpose of over-pressurising the exetainers was to avoid any intake of ambient air into the exetainer if any leaks occurred. Subsequent samples were extracted via the same method at five minute intervals over 20 minutes, resulting in five samples per chamber test. In the winter months, the total test time was extended to 24 minutes, with sampling intervals every six minutes. The sampling time in winter was extended, following other studies (Whalen and Reeburgh, 1988; Laine et al., 2007), because with lower temperatures and lower vegetation cover lower fluxes were expected. Therefore,

a longer test time was needed to ensure that fluxes could be detected. However, with time it was realised that by taking a sample immediately after chamber closure, the air within the headspace had not been sufficiently mixed. Many of the CH_4 concentrations detected in these first samples from each test were significantly higher or lower than the four samples that followed. Therefore, the procedure was altered in April 2012, with the first sample taken three minutes after the chamber was closed. The four subsequent samples were still collected at five minute intervals, resulting in a total test time of 23 minutes for the remainder of the fieldwork period. Approximately 20 seconds before a sample was taken the syringe was pumped up and down three times to ensure that it was purged. At the start (immediately after chamber closure) and end (immediately prior to the last sample collection) of the chamber test, readings of temperature (°C) and barometric pressure (hPa) in the chamber were taken using the Commeter probe. The 20 minute test time during the summer months is likely to have caused artificial warming within the chamber on days with strong sunlight, as described above.

The CH_4 concentration within each gas sample was measured using an Agilent 7890A gas chromatograph (GC), fitted with a flame ionisation detector by staff at the School of Geography at Queen Mary University, London. Prior to the field samples being run through the GC known concentration standards of CH_4 were run through the instrument. After every ten samples, one of the standards was run through the machine to test for any drift in the results. The staff at Queen Mary University never highlighted any problems associated with the drift standards, and so it was assumed that there were no problems, or that the staff corrected for any problems before handing over the results. Over time, the calibrations were stable, and the staff at Queen Mary University, again, never highlighted any problems in this area.

Calibration standards were run at the start of every use of the GC for the samples collected for this project. Standards are used to establish the response (often

termed area under the curve) of the GC to a known concentration. When multiple standards are used, a calibration curve can be plotted using the standard concentrations against their responses, with a trendline fitted to the data. The resulting equation from the trendline was then applied to the data from the samples to obtain their CH_4 concentrations. However, the choice of which trendline to apply and accept for the calibration data was important, as explained below. Only one set of standards was run through the GC from which to make a calibration curve for each GC run, therefore it is unknown if there would have been any variation within the results from the standards; an issue that would have been identified, if present, through multiple injections of the same standards for each GC run.

The standards used to calibrate the GC on a particular run and their resulting responses are shown in Table 3.3. The 0 ppm standard was oxygen-free nitrogen. In this example, from the data produced for the chamber gas samples in this particular GC run, the highest response value from a sample was 5.89, which makes only the first three standards relevant because all the responses from the samples were below the response of the 25 ppm standard (13.91). However, examples will be given here of using all of the standards and only some of the standards for obtaining a calibration equation.

Table 3.3: GC output data of the results from standards

CH_4 standard (ppm)	**Response – area under the curve**
0	1.51
2.5	3.47
25	13.91
50	37.34
99.1	92.99
500	323.69

Figure 3.5 shows the three resulting graphs, trendlines and equations for applying a calibration using all of the standards shown in Table 3.3. The linear trendline (a) has the lowest r^2 value at 0.992, which is still very high; however, the three points in the graph that are of interest are the first three, which the trendline appears to be beneath. The second-order polynomial trendline (b) intersects the three data point of interest much better; however, the third-order polynomial trendline (c) crosses through those three points most accurately and would therefore be the preferred calibration curve.

Figure 3.6 shows the three resulting graphs, trendlines and equations for applying calibrations using the first four of the standards shown in Table 3.3. Four standards were used instead of three because four was deemed to be the minimum number of standards on which to base a reliable calibration curve. Although the third-order polynomial trendline (c) has a seemingly-perfect r^2 value of 1 (or > 0.99999999), the curve in the line that rises above the highest standard of 50 ppm indicated that it should be discarded. From the remaining two graphs, the linear trendline (a) does not cross through the first three points, which are the ones of interest based on the data from the samples. Therefore, from Figure 3.6, the second-order polynomial trendline (b) appears to be the most appropriate.

The differences between the results shown in Figures 3.5 and 3.6 highlight the problems associated with using standards that are well above the range of concentrations found in the samples being analysed. It is recognised that it can be expensive and time-consuming to mix CH_4 standards of specific concentrations low enough to be within the range of field-monitored concentrations. However, the benefits of these actions would have been very useful in this situation. Standards that are higher than the concentrations of interest can skew the calibration curves within the range of concentrations of interest, as shown in Figure 3.5, which necessitates the use of fewer standards, as shown in Figure 3.6. To produce a calibration curve from more than four standards would be beneficial, but only if the

standards were of low enough concentrations to not skew the calibration curve produced.

When comparing the two graphs that have the best r^2 values (Figure 3.5c and Figure 3.6b), Figure 3.5c has the better r^2 value, suggesting that it should be the one to carry forward and apply to the data, which is the approach that was taken with the data for this study. However, to further illustrate the differences in results that these different calibration choices can lead to, five of the six calibration equations were applied to the data from two chamber tests included in this particular GC run. The equation in Figure 3.5a resulted in negative CH_4 concentrations, which is an impossible scenario, and so this result was not carried forward. The equation in Figure 3.6c was discarded due to the high curve in the trendline, as described above. Full details of how fluxes were obtained from CH_4 concentrations produced from GC data are given below in Section 3.2.2.3; however, Table 3.4 shows the resulting CH_4 fluxes calculated for the two chamber tests that had the four calibration equations applied.

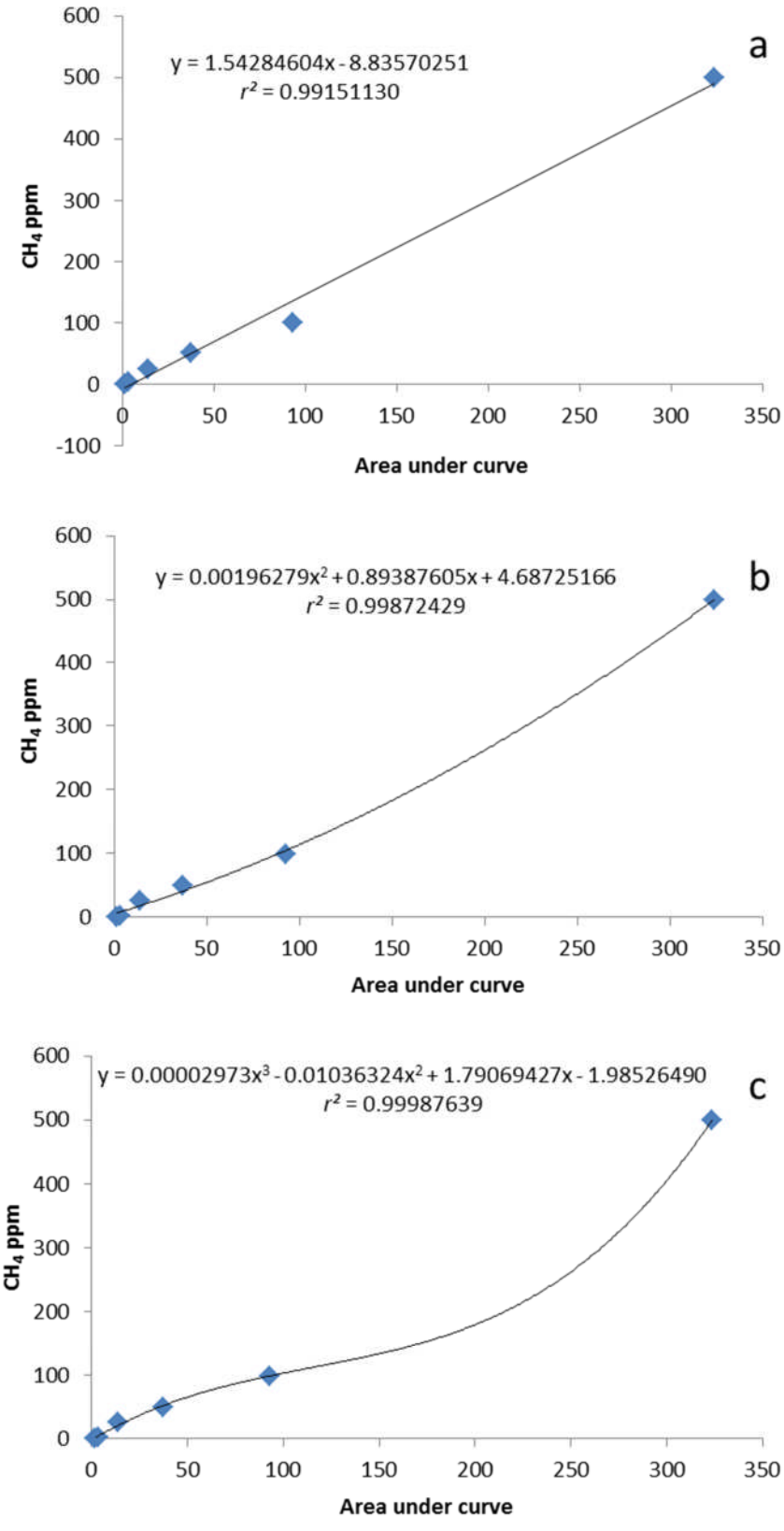

Figure 3.5: GC calibration data using all standards with trendlines and resulting equations for (a) a linear trendline, (b) a second-order polynomial trendline, and (c) a third-order polynomial trendline

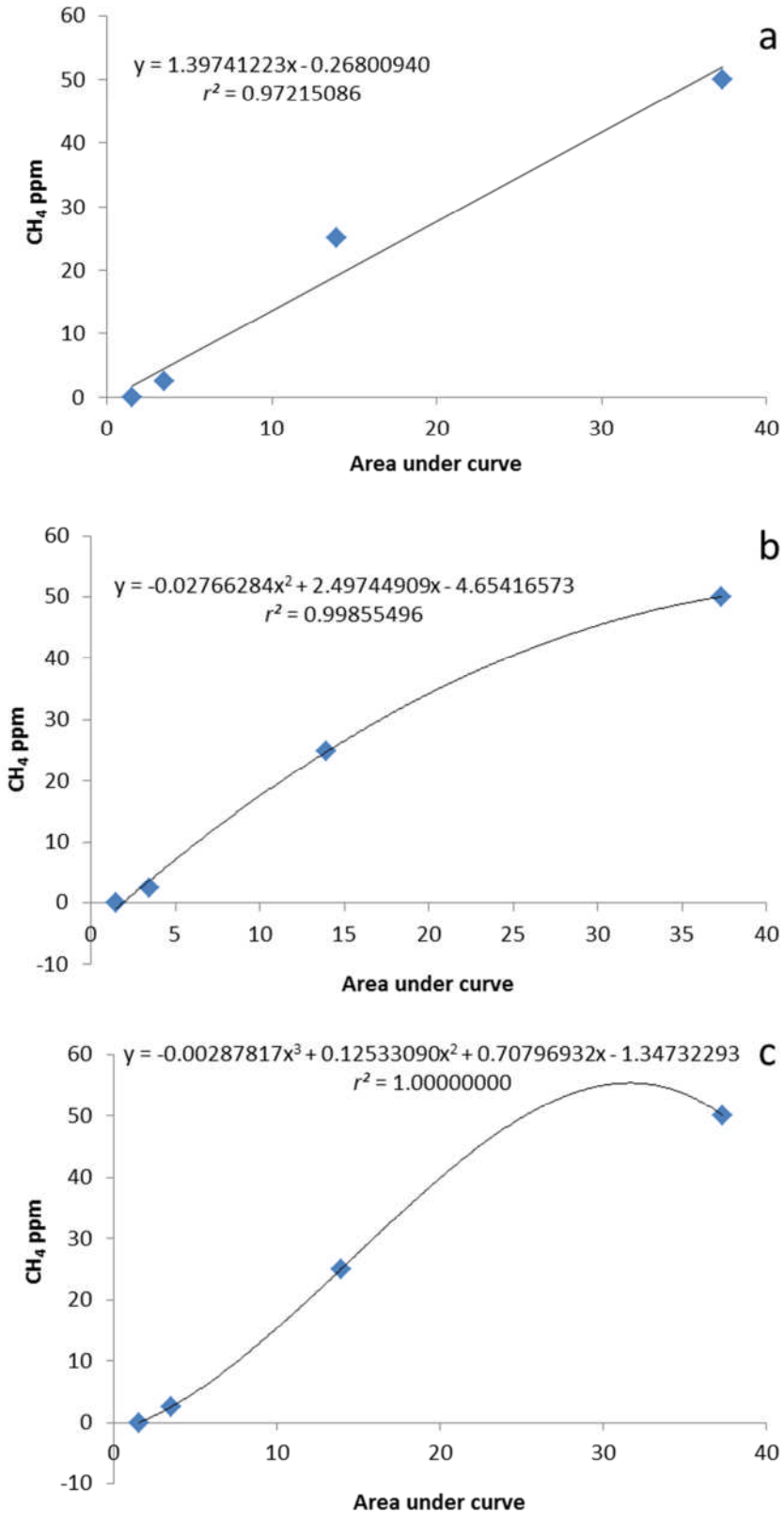

Figure 3.6: GC calibration data using standards 0-50 ppm with trendlines and resulting equations for (a) a linear trendline, (b) a second-order polynomial trendline, and (c) a third-order polynomial trendline

As Table 3.4 shows, a wide range of fluxes can be produced for one collar depending on the calibration equation chosen from the GC output. Overall, for example collar 1 the difference between the minimum and maximum flux estimated in Table 3.4 was 12.2 mg CH_4 m^{-2} day^{-1}, and for example collar 2 this difference was 36.4 mg m^{-2} day^{-1}. Of the two equations that were deemed most suitable (Figure 3.5c and Figure 3.6b) there was a difference of 5.5 mg CH_4 m^{-2} day^{-1} for collar 1 and 10.2 mg CH_4 m^{-2} day^{-1} for collar 2. This difference in fluxes shows that the choice of calibration equations can have an impact on not only the fluxes calculated for each collar, but also on any seasonal or annual fluxes calculated from the data.

Table 3.4: Resulting fluxes from the calibration equations in Figures 3.5 and 3.6

Calibration equation (referred to by Figure reference)	**Example collar 1**	**Example collar 2**
	Fluxes expressed in mg CH_4 m^{-2} day^{-1}	
Figure 3.5b	10.8	24.9
Figure 3.5c	17.5	51.1
Figure 3.6a	14.6	38.4
Figure 3.6b	23.0	61.3

For CO_2 measurements, the IRGA was connected to the chamber, as shown in Figure 3.4. The IRGA pumps gas from the chamber headspace at approximately 350 ml min^{-1}. As Figure 3.5 shows, the IRGA has both intake and outlet tubes, which were offset within the chamber in order to reduce the chance of the same air sample continually passing through the IRGA. In the same way as for the CH_4 sampling, the chamber was placed into the water-filled gutter of the collar or extension collar, closing the headspace and starting the measurements.

Initially, readings of the CO_2 concentration within the chamber were taken as soon as the chamber was sealed and then every 20 seconds for a total of 120 seconds. However, as with the CH_4 sampling, it was realised that the air within the chamber was not sufficiently mixed, to ensure a representative sample, at the initial chamber seal time, and example of which is shown in Figure 3.7. Therefore, from April 2012, the first reading was not taken until 20 seconds after the chamber closure, extending the total test time to 140 seconds. There is also a chance that as well as an insufficient mixing time, the initial reading at the chamber seal time could have been from ambient air housed within the inlet tube to the IRGA. The IRGA ran continuously between chamber tests, and so the pumping volume of the instrument may not have been strong enough to process and dispel the last sample of ambient air as the chamber test began and the first reading was taken.

At the start (immediately after chamber closure) and end (immediately prior to the last measurement) of the chamber test, readings of temperature and barometric pressure in the chamber were taken from the Commeter probe. Chamber CO_2 measurements were conducted twice for each collar on each field visit, once with the chamber shroud removed to allow light penetration into the chamber for estimation of NEE, and once with the chamber shroud in place to prevent light penetration for estimation of ecosystem respiration.

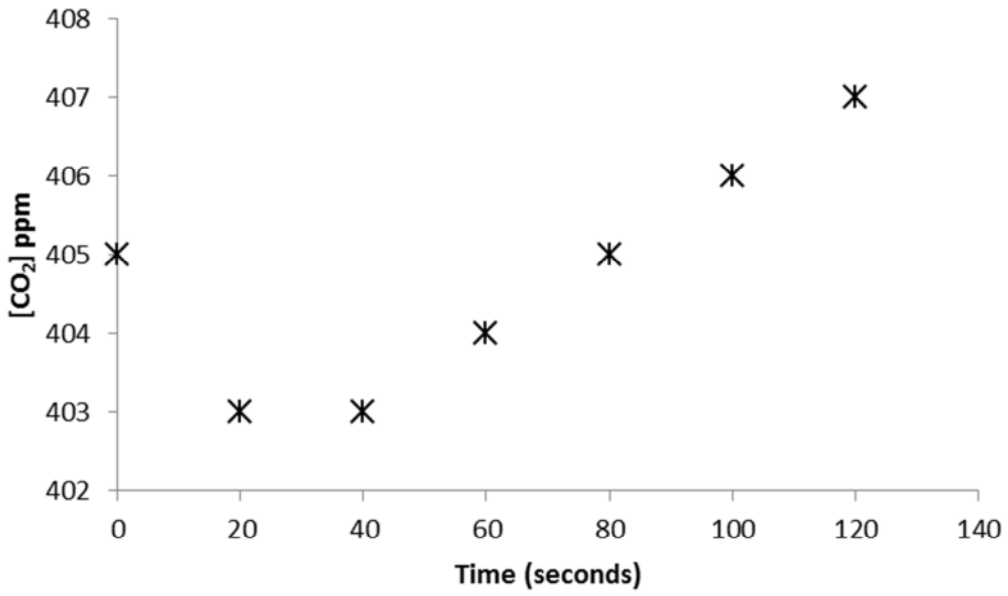

Figure 3.7: An example of IRGA data showing insufficient initial mixing within the chamber

3.2.2.4 Flux calculations

Fluxes were calculated using a spreadsheet developed by Prof. Andy Baird and Dr. Sophie Green for the Defra SP1202 project[1]. The flux calculation was based on a modified version of Equation 3.2:

$$\boldsymbol{F_g = \frac{1}{A}\frac{dg_m}{dt}} \qquad \textbf{Equation 3.3}$$

where F_g is the gaseous flux in mg m^{-2} day^{-1}, g_m (mg) is the mass of the chamber gas (calculated by V x ρ_g as in Equation 2) and all other components are as in Equation 2. The field and laboratory data required for flux calculations were the concentrations of CH_4 (ppm) from the gas samples, the measurements of CO_2

[1] For more information see http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=16991

(ppm) concentrations, the temperature and barometric pressure readings from inside the chamber at the start and end of the chamber tests, the surface area covered by the collar and the volume of the chamber headspace. The chamber headspace volume should include any area between the peat surface and the top of the collar protruding from the peat surface, as well as the actual chamber volume. Also required for a flux calculations were values of standard temperature (K) and pressure (kPa) (STP), the volume of one mole of the gas of interest under STP and the molecular mass of the gas of interest. All of this subsequent information was as per the International Union of Pure and Applied Chemistry.

The spreadsheet calculations work as follows. First, for each CH_4 sample or CO_2 measurement taken in the chamber test, the volume (m^3) of the gas relative to the chamber volume was calculated. This volume was then converted to the equivalent volume (m^3) of the gas at STP, which was then converted into moles of gas, and finally into a mass (mg). An ordinary least-squares linear regression was applied to the mass data for each chamber test, which gave a rate for the gas: an increase (positive value) if gas was being lost from the peat to the atmosphere, and a decrease (negative value) if there was gas uptake by the peat, or the vegetation. The regression was applied to mass data expressed over the time of the chamber test, which accounts for the dg_m/dt part of Equation 3. However, there were criteria that had to be met for this resulting rate to be converted to a flux. The gradient of the rate of change had to be significant, and the r^2 value of the regression had to be greater than 0.8. If these two criteria were met, then the final part of Equation 3.3 was applied to the data: $1/A$, where 1 is replaced by the slope coefficient from the regression applied to the mass data. The final result was the mass flux density (F_g) in mg m^{-2} day^{-1}.

The spreadsheet also accounted for zero fluxes. If the difference between the maximum and minimum CH_4 concentrations sampled from the chamber was lower than 0.3 ppm, then a flux of zero was returned. For CO_2 measurements, this

threshold concentration change was 1 ppm. If the rate of mass change within the chamber could not be fitted with a significant straight line with $r^2 > 0.8$ and did not fit the criteria for a zero flux, the chamber test was rejected and no flux recorded

On three occasions, ebullition events were detected within the results of CH_4 chamber tests. The chamber tests in question were from collar A1 on 20/06/2012, collar B1 on 18/07/2012 and collar B5 on 14/08/2012, as shown in Figure 3.8. Ebullition events were identified via the CH_4 concentration detected in the sample when analysed via GC. The change in CH_4 concentration during a chamber test was expected to be roughly linear, and so the resulting concentrations were plotted to check that this was the case. The concentrations of any samples that were outside of the expected linear trend were scrutinised to deem if they could be the result of an ebullition event. In these cases, depending on the timing of the ebullition event, the samples before or after were excluded from the flux calculations in order to prevent pre- and post-ebullition concentrations being included in the same flux calculation, as shown in Figure 3.8, where the hollow data points are the excluded ones. Five samples were taken in each chamber test. In collar A1 the ebullition event was detected in the first sample, meaning that this first sample was excluded and the remaining four post-ebullition samples were used to calculate the flux. In collar B1, the ebullition event was detected in the fifth sample, so that sample was excluded and the remaining four pre-ebullition samples were used to calculate the flux. In collar B5, the second sample contained the evidence of the ebullition event, and the concentration in the third sample was lower as mixing of the ebullitive release occurred within the chamber. Therefore, the first and second samples were excluded and the remaining three post-ebullition samples were used in the flux calculation. These two flux calculations using ebullition event data at Site B were then the two highest fluxes recorded throughout the entirety of the fieldwork period

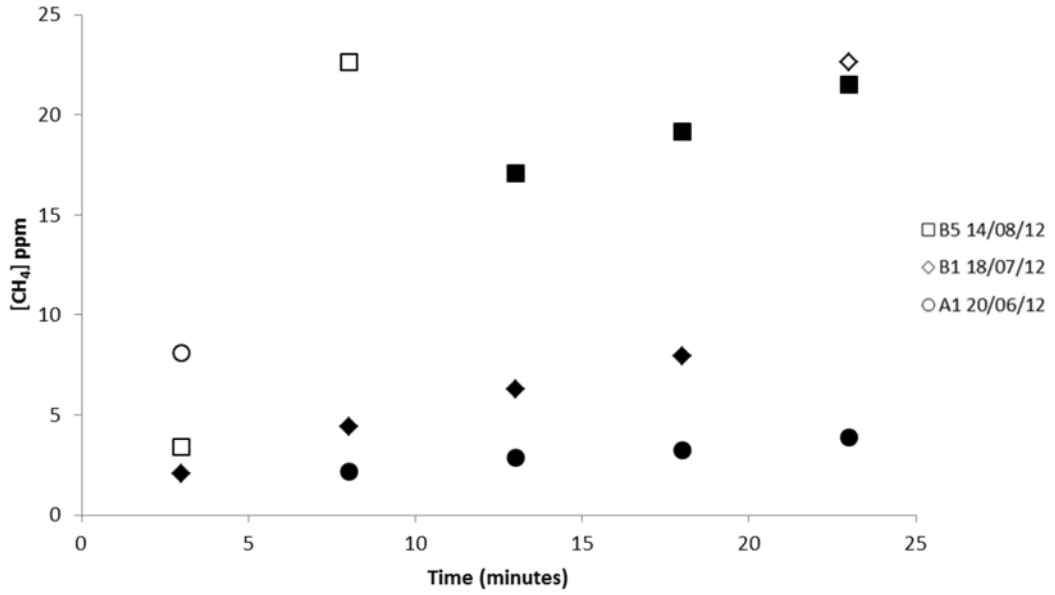

Figure 3.8: Chamber test results where ebullition events occurred

3.2.2.5 Ebullition funnels

Inverted funnels, sometimes termed ebullition funnels and often made from glass, can be used to capture the release of CH_4 from peat to the surface of the water table in bubble form (Belger et al., 2011; Stamp et al., 2013; Strack et al., 2005; Strayer and Tiedje, 1978). If the air in the funnel is removed and the water beneath is drawn up inside the funnel, any gas bubbles that are released from beneath the funnel will displace the water within the funnel and collect at the top. Samples of this gas can then be extracted from the funnel and analysed for CH_4 concentrations and, in combination, the volume flux data and the CH_4 concentration can give a CH_4 mass flux due to ebullition.

Ebullition funnels, constructed from glass, were deployed this study to collect CH_4 emissions in bubble form. However, problems with the resulting data were encountered, and so the data was considered to be of insufficient quality to be included in this thesis. It is therefore recognised that any fluxes reported on a site

basis in this study may be conservative estimates, because potential ebullitive fluxes are not included.

3.2.3 Environmental and meteorological variables

3.2.3.1 Environmental variables

Soil temperatures were measured using Hanna soil temperature probes. On each fieldwork visit the soil temperature in the centre of each collar was measured at 9 cm depth (determined by the length of the probe) prior to the start of chamber tests.

To measure water table position, dipwells were constructed from 32 mm (internal diameter) UPVC pipe. Holes of 8 mm diameter were drilled into the pipe at vertical increments of 10 cm. Four columns of holes were drilled into the pipe, at a 5 cm offset, as shown in Figure 3.9. Each dipwell had a lid to prevent any insects entering the pipe. In order to allow for air to escape the dipwell when water was flowing in, one hole (8 mm diameter) was drilled into the top of the pipe (above-ground once installed), as shown in Figure 3.9. Each of these holes was covered in a fine mesh prior to field installation, to prevent any insects entering the pipe. The base of each dipwell was covered in duct tape to avoid any peat entering the dipwell from underneath during installation.

Dipwells were installed using a screw auger of approximately the same diameter as the dipwells. Each dipwell was located within approximately 50 cm of its adjacent collar to monitor the WTP within the vicinity of the collar. Firstly a test hole was augered approximately 1 m from the collar to determine the depth of the boundary between the peat and the mineral layer below. The hole for the dipwell was then augered to a depth just short of this mineral layer. The dipwell was then gently pushed into the hole in order to try and minimise any smearing of the peat on the sides of the hole that could impede water flow. Due to the very low water-

table positions at each site at the time of installation, the dipwells could not be flushed to remove any debris that may have entered the dipwell pipe through the holes in the sides upon installation. Any of the holes drilled into the dipwell that were above ground after installation were covered in duct tape to prevent insects entering the pipe, with the exception of the mesh-covered hole near the top of the dipwell.

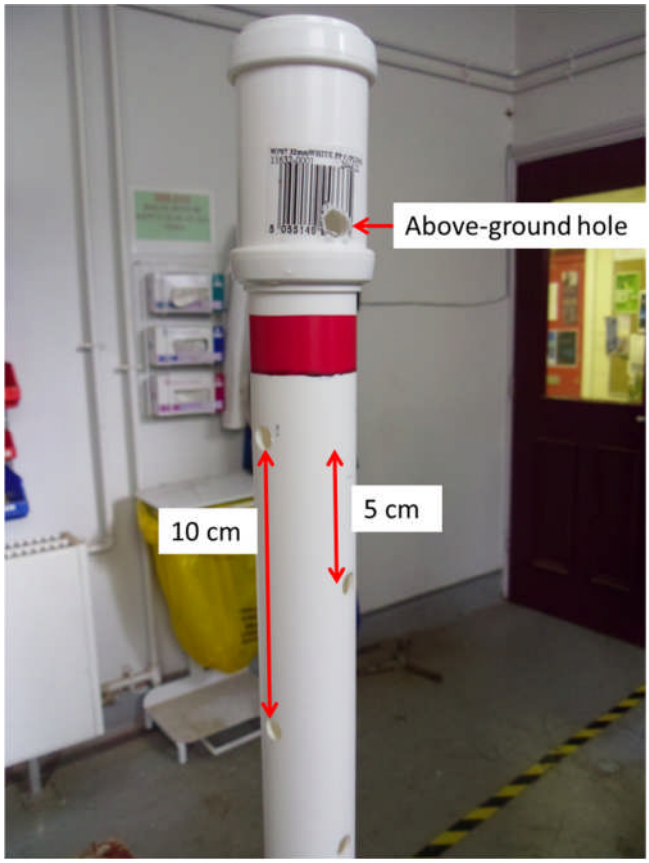

Figure 3.9: An example of a dipwell (mesh not attached to above-ground hole)

To measure the water-table position within the dipwells, the distance from the peat surface to the top of the dipwell was measured. Then a bubble tube was used to determine the distance from the top of the dipwell to the water table within the dipwell. The bubble tube was simply a piece of plastic tubing attached to a bamboo cane with cable ties. The end of the bubble tube was lowered into the dipwell, with the operator blowing through the top of the plastic tubing. The

sound of the water bubble indicated that the end of the bubble tube had reached the water table. After measuring how far the bubble tube was inserted into the dipwell before the water table was reached, this distance was subtracted from the earlier measurement of the length of the dipwell protruding from the peat surface to obtain a water-table position, where a positive value indicated the depth of water above the peat surface (strictly surface inundation rather than a water table), and a negative value indicated the depth of the water table beneath the peat surface.

3.2.3.2 Meteorological variables

An AWS (Vantage Pro2, Davis Instruments, USA) was installed close to Site A (NGR: SE 72175 16734) to measure a variety of meteorological variables: air temperature (precision 0.1 °C; accuracy ± 0.5 °C), relative humidity (precision 1 %; accuracy ± 3 % (4 % if > 90 %)), wind speed (precision 0.4 m s^{-1}; accuracy ± 1 m s^{-1}), barometric pressure (precision 0.1 hPa; accuracy ± 1.0 hPa), rainfall (precision 0.2 mm; accuracy ± 0.2 mm), solar radiation (precision 1 W m^{-2}; accuracy ± 5 % of full scale) and potential evapotranspiration (precision 0.1 mm; accuracy ± 0.25 mm) (estimated using air temperature, relative humidity, average wind speed and solar radiation data) . Data from the AWS were averaged or calculated (depending on the variable) at 60 minute intervals.

3.3 Limitations and missing data

Soil temperatures and water-table positions were only measured manually whenever a field visit was made. However, if each of these variables had been continuously logged in at least one location on each site then there would have been a more complete environmental data set to support the meteorological variables collected via the AWS.

During the summer of 2012, the AWS had several periods of partial power failure, resulting in the loss of some data, most importantly air temperature. A nearby farm had the same type of AWS located approximately 3.1 km from the AWS for this project. It was possible to obtain the data from the farm AWS and produce a relationship (r^2 = 0.92) from which to predict air temperature during the periods of power failure.

If there was heavy precipitation, CO_2 sampling could not be conducted due to the risk of damaging the IRGA through water uptake. There were also instances of IRGA battery failure that meant several flux tests were not conducted. In late September and early October 2012 road closures prevented access to Site D, resulting in the cancellation of two planned data collection visits. Table 3.5 shows data on the amount of chamber flux tests aimed for, achieved and accepted for each type of test. Overall, 93.6 % of the CH_4 flux tests aimed for were completed, 71.9 % of the NEE flux tests and 71.4 % of the respiration flux tests.

The data collected via the methods described above are presented in Chapter 4, where any relevant statistical analyses applied to the data will also be presented. Modified or different methods were used to obtain the results presented in Chapters 5 and 6, and so these methods and analyses will be detailed in the corresponding chapters.

Table 3.5: Numbers of chamber flux tests aimed for, completed and accepted (referring to if flux spreadsheet passed criteria)

(a) Methane fluxes			
Site	**Aimed for**	**Completed**	**Accepted**
A	138	130	118
B	138	132	117
C	138	135	87
D	138	120	89
(b) NEE fluxes			
Site	**Aimed for**	**Completed**	**Accepted**
A	138	105	95
B	138	98	86
C	138	106	93
D	138	88	80
(c) Respiration fluxes			
Site	**Aimed for**	**Completed**	**Accepted**
A	138	105	102
B	138	98	95
C	138	105	99
D	138	86	81

Chapter 4: Annual and seasonal fluxes of methane and carbon dioxide and their drivers

4.1 Introduction

4.1.1 Overview

Chamber flux measurements of CH_4 and CO_2 provide an insight into the gaseous carbon budgets of peatlands, and are often calculated in mg m^{-2} day^{-1}. However, it is often useful to have gaseous carbon budgets reported over longer timescales; from seasonal to annual and beyond. Policies relating to peatland management cover these longer timescales, and so for these policies to include methods aiming to reduce the global warming potential (GWP), knowledge of gaseous fluxes over seasonal and annual timescales is beneficial. Also, the response times of peatlands to land use changes, such as restoration, are unlikely to be evident on a day-to-day basis, but rather on seasonal and annual timescales.

Chamber flux measurements are 'snapshots' in time but various methods are available to fill in the gaps between measurements. For CO_2 fluxes, due to the strong and well-established influence of PAR, a modelling approach is often taken (Samaritani et al., 2011; Waddington et al., 2010). However, with CH_4 fluxes the drivers are not so clear, therefore, interpolation or weighted-total approaches are often used for gap-filling (Dise et al., 1993; Hargreaves and Fowler, 1998; Whalen and Reeburgh, 1992).

The hypothesis proposed by Joosten et al. (2006), as detailed in Section 2.2.2 and shown in Figure 2.3, suggests that within the 5-50 years following restoration, a peatland will be a net source of carbon, but will then become a net sink of carbon. If the best-case scenario proposed by Joosten et al. (2006) is correct, and can be applied to peatlands outside of Belarus, then of the four field sites chosen for this

study, Sites A and B could already be a net carbon sink and Sites C and D would both still be net carbon sources. The hypothesis presented by Bain et al. (2011), as detailed in Section 2.2.2 and shown in Figure 2.4 suggests that restored peatlands in the UK will initially be a net carbon source, but within ten years of restoration should become a net carbon sink. If this hypothesis is correct, then Site A could already be sequestering carbon, with Site B being very close to making the switch from a source to a sink; Sites C and D would still be net carbon sources.

Holman and Kechavarzi (2010) estimated the gaseous carbon budget of the Humberhead peatlands based on reported fluxes in the literature for similar areas and conditions. Two different rewetting scenarios were considered; a seasonally-varying water table and a high stable water table (Holman and Kechavarzi, 2010). In the scenario with seasonal variation in the water-table position, there was an estimated net carbon loss, with a predicated annual losses of CO_2 at 1.5-5 kg m^{-2} yr^{-1} and CH_4 at 30-2000 mg CO_2-e m^{-2} yr^{-1} (Holman and Kechavarzi, 2010). A high stable water table scenario resulted in a net carbon gain, with CO_2 uptake between 0.07 and -0.5 kg m^{-2} yr^{-1}, which counteracted the loss of CH_4 as CO_2-e of 4.4-47 g m^{-2} yr^{-1} (Holman and Kechavarzi, 2010).

4.1.1.1 Aim

This chapter will address research questions 1 and 2:

1. **Do CH_4 and CO_2 emissions from peatlands change with time following restoration?**
2. **What are the main drivers of CH_4 and CO_2 emissions in restored peatlands?**

Fluxes of CO_2 and CH_4 at Thorne and Hatfield Moors were measured over 13 months (late September 2011 to late October 2012) using static closed chambers, as described in Section 3.2. Data collected over the 12 month period of late

October 2011 to late October 2012 will be presented, and reasons for the selection of these 12 months is explained in Section 4.2.2.1.

Models for CO_2 fluxes were applied on a per-collar basis, but were not successful for every collar. A weighted-total approach was used to give seasonal and annual CH_4 fluxes per collar. These CH_4 fluxes were also converted to CO_2-e and added to the annual CO_2 fluxes that were successfully modelled to give the GWP for those collars. The results can be compared to the predictions of Holman and Kechavarzi (2010). Multiple regression analyses were used to identify CH_4 flux drivers, and the modelling results were used to provide information on CO_2 flux drivers.

4.1.2 Approaches to calculating annual and seasonal gaseous fluxes

4.1.2.1 Carbon dioxide

Table 4.1 shows that, overall, many studies that model CO_2 fluxes to calculate NEE for restored peatlands take similar approaches. Both NEE and ecosystem respiration (termed total respiration)(R_{TOT}) are measured using static closed chambers and an infrared gas analyser (IRGA) in the majority of the studies in Table 4.1. A light chamber is used for NEE measurements, and a shrouded chamber is used for R_{TOT} measurements. Gross photosynthesis (P_G) and R_{TOT} can be modelled to provide annual estimates of NEE. If P_G and R_{TOT} are reported as absolute values, NEE is given by:

$$NEE = P_G - R_{TOT} \qquad \textbf{Equation 4.1}$$

and then P_G can be calculated thus:

$$P_G = NEE + R_{TOT}$$

In the literature, as shown in Table 4.1, the most commonly-adopted approach to modelling P_G is to use a model such as that used by Tuittila et al. (1999):

$$P_G = Q * I/(I + k) * EV * ETI * T_{-5}$$ **Equation 4.2**

where Q is the asymptotic maximum coefficient, I is solar irradiance (W m^{-2}), k is the half-saturation constant, EV is the percentage of *Eriophorum vaginatum* cover, ETI is the effective temperature sum index (°C) and T_{-5} is the soil temperature (°C) at 5 cm depth. The ETI is a variable to represent the growing season, and was calculated by dividing the cumulative temperature sum by the number of temperature sum days over the growing season (Tuittila et al., 1999). The model structure is based on the relationship between P_G and I, represented by the rectangular hyperbola using coefficients Q and k, where Q is reliant on the remaining model parameters of EV, ETI and T_{-5} (Tuittila et al., 1999)

Bellisario et al. (1998), Marinier et al. (2004) Samaritani et al. (2011), Waddington et al. (2010) and Wilson et al. (2007) all use variations of Equation 4.2 to model P_G. For example, Samaritani et al. (2011) uses PAR instead of solar irradiance, and includes variables of air temperature and WTP instead of EV, ETI and T_{-5}. Regardless of the differences in the chosen variables, all variations of Equation 4.2 retain the quotient, which produces a rectangular hyperbola. Figure 4.1 shows an example of this rectangular hyperbola using data from this study using Equation 4.2 (Tuittila et al., 1999).

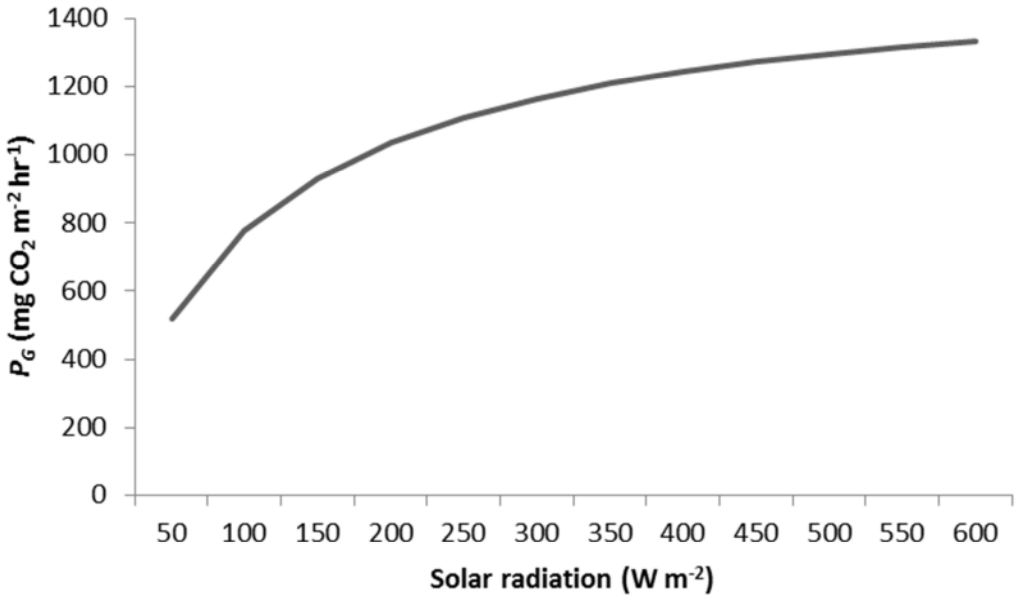

Figure 4.1: An example of the response of P_G to changes in solar radiation using Equation 4.2

The most common approach to modelling R_{TOT}, found in Table 4.1 is through an additive model formed through linear regression, as shown in this example from Kivimäki et al. (2008):

$$\ln R_{TOT} = b0 + b1 * EV + b2 * T_{-5} + b3 * WTP + b4 * ETI + b5 * (EV * WTP)$$

Equation 4.3

where ln is the natural logarithm and all other variables are as in Equation 4.2. Both Tuittila et al. (1999) and Samaritani et al. (2011) modelled the logarithm of R_{TOT}, whereas the other studies shown in Table 4.1 modelled R_{TOT} itself. Soil temperature is the environmental variable most-frequently found in the R_{TOT} models detailed in Table 4.1, with the exception of Bellisario et al. (1998). Other variables include WTP (Bellisario et al., 1998; Marinier et al., 2004; McNeil and Waddington, 2003; Samaritani et al., 2011; Tuittila et al., 1999), air temperature (Bellisario et al., 1998; Samaritani et al., 2011) and volumetric soil moisture content (Waddington et al., 2010).

Table 4.1: Studies of NEE on restored peatlands. Positive values indicate CO_2 release to the atmosphere, negative values indicate CO_2 uptake from the atmosphere. Definitions of symbols used can be found at the end of the table.

Reference	**NEE** **(g CO_2-C m^{-2})**	**Vegetation**	**Location**	**Duration of study**	**Flux measurement method**	**CO_2 modelling method**
Bellisario et al. (1998)	Daily: -5 to 3 g CO_2-C m^{-2} day^{-1} Average: 1.4 to 2.5 g CO_2-C m^{-2} day^{-1}	*Sphagnum riparium, Carex* spp., *Vaccinium oxycoccus, Andromeda glaucophylla, Menyanthes trifoliata, Camplyium stellatum, Calliergon stramineum*, brown mosses	Bog/fen near Thompson, Manitoba	June-September 1994	Static chambers and IRGA to measure NEE and R_{TOT}	Modelled relationship between P_G and PAR using a variation of Equation 4.2. R_{TOT} modelled with linear regression using WTP and/or air temperature
Marinier et al. (2004)	P_G: -21.6 to -81.6 g CO_2-C m^{-2} day^{-1} R_{TOT}: 2.4 to 31.2 g CO_2-C m^{-2} day^{-1}	Bare peat and *Eriophorum vaginatum*	Near Shippagan, New Brunswick and Rivière-du-Loup, Quebec	3 growing seasons May-October	Static chambers and IRGA to measure NEE and R_{TOT}	Modelled relationship between P_G and PAR using a variation of Equation 4.2. R_{TOT} modelled with linear regression using WTP and temperature

Reference	**NEE** **(g CO_2-C m^{-2})**	**Vegetation**	**Location**	**Duration of study**	**Flux measurement method**	**CO_2 modelling method**
McNeil and Waddington (2003)	Study period: 575 Seasonal R_{TOT}: 127 Bare peat: 84	*Sphagnum capillifolium*, *Picea mariana*, Ledum groenlandicum, *Vaccinium angustifolium*, *Kalmia angustifolia*, *Chamaedaphne calyculata*	Cacouna Bog, Quebec	May-August, October 2000	Static chambers and IRGA to measure NEE and R_{TOT}	R_{TOT} modelled using linear regression with WTP and soil temperature. Photosynthesis determined via plant removal and comparison of fluxes.
Petrone et al. (2001)	478	Restoration via various methods in 1999	Bois-des-Bel peatland, Quebec	May-October 2000	Eddy covariance	Night-time fluxes used to define R_{TOT} within NEE then R_{TOT} modelled as a function of soil temp

Reference	**NEE** **(g CO_2-C m^{-2})**	**Vegetation**	**Location**	**Duration of study**	**Flux measurement method**	**CO_2 modelling method**
Samaritani et al. (2011)	40	*Sphagnum fallax, Eriophorum vaginatum, Carex nigra, Comarum palustre, Polytrichum commune*	Cutover bog, Swiss Jura Mountains	One growing season	Static chambers and IRGA to measure NEE and R_{TOT}	P_G modelled using a variation of Equation 4.2 R_{TOT} log-transformed and modelled using linear regression with WTP, soil temperature at 30 cm and air temperature
	Average: -222	*Sphagnum fallax, Eriophorum vaginatum, Potentilla erecta*				
	Average: 209	*Sphagnum fallax, Eriophorum vaginatum, Polytrichum commune, Vaccinium oxycoccos*				

Reference	**NEE** **(g CO_2-C m^{-2})**	**Vegetation**	**Location**	**Duration of study**	**Flux measurement method**	**CO_2 modelling method**
Tuittila et al. (1999)	Rewetted: submerged = -9.1 to -64.5 Not submerged = 26.1 to 44.1	*Eriophorum vaginatum*, bare peat	Cutover peatland Aitoneva, Kihniö, Finland	Growing seasons 1994-1997	Static chambers and IRGA to measure NEE and R_{TOT}	P_G modelled using Equation 4.2 R_{TOT} log-transformed and modelled using linear regression with EV, T_{-5}, WTP, ETI and $ETI * WTP$
	Control: low *E. vaginatum* cover = 41.8 to 95.3 High *E. vaginatum* cover = 52.1to 109.9					

Reference	**NEE** **(g CO_2-C m^{-2})**	**Vegetation**	**Location**	**Duration of study**	**Flux measurement method**	**CO_2 modelling method**
Waddington et al. (2010)	Pre-restoration: 245	Only 23 % vegetation cover: *Picea mariana, Betula* spp.	Bois-des-Bel peatland, Quebec	May-early October 1999 (pre-restoration), 2000-2002 (post restoration)	Static chambers and IRGA to measure *NEE* and R_{TOT}	P_G modelled using a variation of Equation 4.2 R_{TOT} modelled using multiple linear regression using soil temperature at 2, 5 and 10 cm depth and volumetric soil moisture content
	2 years post-restoration: -15 to -25	*Polytrichum* spp., Ericaceous sp, *Eriophorum vaginatum, Typha latifolia, Sphagnum* spp.				
Wilson et al. (2007)	2002: 163 to 651	*Phalaris arundinacea, Typha latifolia, Eriophorum angustifolium, Bryum* sp., *Holcus lanatus, Juncus effusus*	Turraun, Ireland	April 2002 – December 2003	Static chambers and IRGA to measure NEE and R_{TOT}	P_G modelled using a variation of Equation 4.2 R_{TOT} log-transformed and modelled using linear regression with soil temperature at 5 cm depth, WTP and VGA
	2003: 308 to 760					

4.1.2.2 Methane

Table 4.2 shows results from studies which have presented annual CH_4 fluxes. Most of these studies involved field measurements of CH_4 fluxes over at least a one year period; however, in some studies (Crill et al., 1988; Hargreaves and Fowler, 1998; Pelletier et al., 2007; Roulet et al., 1992) field measurements were taken for less than one year, usually just in the summer months. Pelletier et al. (2007) conducted static closed chamber tests between June and August 2003, with additional tests carried out during one week in November 2003 and one week in March 2004. Hargreaves and Fowler (1998) measured CH_4 fluxes via eddy covariance for only two weeks; however, a weather station was in place near the field site for two years prior to the flux measurements allowing for an annual flux calculation based on linear regression. Roulet et al. (1992) made the assumption that from mid-November to April, CH_4 fluxes would be zero, and so the fluxes reported as annual totals only included May to mid-November. The field measurements by Jackowicz-Korczyński et al. (2010) and Moore and Knowles (1990) were each completed over two years; however, neither study measured or included winter fluxes in their annual flux calculations. Martikainen et al. (1995); Pelletier et al. (2007) and Strack and Zuback (2013) conducted studies where field measurements were concentrated on summer months, but did recognise that there may be some winter fluxes by including at least one set of field measurements in winter months. Given the different time scales of field measurements used in the different studies in Table 4.2, comparisons between the reported fluxes may be limited.

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Cooper et al. (2014)	Pre-drainage mean: 6	*Calluna vulgaris, Eriophorum* spp., *Juncus* spp., *Sphagnum* spp.	Llyn Serw, Migneint blanket bog, Wales	2.25 years	Static closed chambers	Time-weighted average of seasonal subset mean fluxes
	Post-drainage mean: 4.4					
Crill et al. (1988)	Forested bog: 12	*Picea mariana*	Marcell Experimental Forest and Red Lake peatland, Minnesota, USA	3 months	Static closed chambers	Multiplied mean June flux by an assumed season of 150 days
	Open bog: 44	*Sphagnum* spp., *Carex* spp.				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Dise et al. (1993)	Hummock: 3.5 Hollow: 13.8	*Picea mariana, Sphagnum angustifolium, Sphagnum magellanicum, Rhododendron groenlandicum*	Marcell Experimental Forest, Minnesota, USA	2 years	Static closed chambers	Integrating daily fluxes over the year
	Fen lag: 12.6	*Alnus rugosa, Sphagnum* spp.*, Calla palustris, Lycopus uniflorus, Equisetum fluviatile, Viola* spp.				
	Open bog: 43.1	*Chamaedaphne calyculata, Sphagnum capillifolium, Carex oligosperma, Eriophorum virginicum*, *Rhynchospora alba*				
	Open poor fen: 65.7	*Carex oligosperma, Scheuchzeria palustris, Vaccinium oxycoccus, Sphagnum* spp.				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Frolking and Crill (1994)	1991: 68.8 1992: 69.8	*Sphagnum* spp., *Carex* spp., *Chamaedaphne calyculata*, *Vaccinium corymbosum*, *Kalmia angustifolia*, *Kalmia polifolia*, *Rhododenron canadense*	Sallie's fen, New Hampshire, USA	2.5 years	Static chambers	Unclear, but assumed to be an accumulation of monthly average fluxes
Hargreaves and Fowler (1998)	6.9	Not stated	Blanket bog, Caithness, Scotland	2 weeks	Eddy covariance	Extrapolation of linear regression and water-table depth, then scaled according to temperature

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Jackowicz-Korczyński et al. (2010)	2006: 24.5 2007: 29.5	*Eriophorum vaginatum*, *Sphagnum* spp., *Eriophorum angustifolium*, *Betula pubescens*	Stordalen, subarctic Sweden	May-December in 2 years	Eddy covariance	Relationship between soil temperature at 3 cm depth and CH_4 flux used for gap-filling

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Laine et al. (2007)	Hummock: 3.3 ± 0.5	*Racomitrium lanuginosum, Sphagnum rubellum, Sphagnum papillosum, Calluna vulgaris, Erica tetralix* and *Molinia caerulea*	Lowland blanket bog, Glencar, Ireland	2 years	Static chambers	Nonlinear regression modelling
	Hollows: 3.5 – 13 ± 0.1	*Sphagnum cuspidatum, Sphagnum auriculatum, Menyanthes trifoliata, Schoenus nigricans, Carex limonsa*, *Eriophorum angustifolium*				
	High lawn: 5.8 ± 1.1	*Schoenus nigricans, Molinia caerulea, Erica tetralix*, *Rhynchospora alba*				
	Low lawn: 6.1 ± 1.4	*Rhynchospora alba*				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Martikainen et al. (1995)	1991: 18 1992: 43	Virgin fen: *Sphagnum papillosum, Sphagnum angustifolium, Sphagnum fallax, Sphagnum magellanicum*	Lakkasuo mire complex, Finland	2 years, only 1 winter measurement	Static closed chambers	Calculated from monthly emission averages
	1991: -0.03 1992: 0.04	Drained fen: *Pleuzorium schreberi*				
	1991: 5 1992: 2.5	Virgin bog: *Sphagnum angustifolium, Sphagnum fuscum, Empetrum nigrum*, *Sphagnum russowi*				
	1991: 3 1992: 1.5	Drained bog: *Sphagnum russowi, Pleuzorium schreberi* , *Eriophorum vaginatum*				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Moore and Knowles (1990)	1.3 - 9.9	Subarctic fens: *Sphagnum lindbergii, Carex limosa, Carex rariflora, Scirpus cespitosus, Chamaedaphne calyculata, Betula michauxii*, *Menyanthes trifoliata*	Peatlands in Quebec, Canada	2 years, excluding winter	Static chambers	Integration of seasonal pattern.
	1.2 - 4.2	Swamps: *Betula alleghaniensis, Tsuga Canadensis*, *Populus deltoids*				
	0.1	Bogs: *Sphagnum* spp., *Rhododendron* spp., *Betula populifolia*				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Nykänen et al. (1998)	1.0	Palsa: *Vaccinium vitis-idaea, Betula nana, Empetrum nigrum, Rubus chamaemorus, Ledum palustre, Dicranum polysetum, Andromeda polifolia, Cladina rangiferina, Cladonia* spp.	Palsa mire, subarctic Finland	2 years	Static closed chambers	Mid-June – mid-September: summing weekly mean fluxes then multiplying by hours of the week Mid-September – mid-June: extrapolation
	24.7	Palsa margin: *Sphagnum riparium, Eriophorum angustifolium*, *Eriophorum russeolum*				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Pelletier et al. (2007)	3.8	*Sphagnum fuscum, Chamaedaphne calyculata, Rubus chamaemorus, Rhododendron groenlandicum, Sphagnum balticum, Sphagnum pulchrum, Carex* spp., *Cladonia stellaris, Sphagnum lindbergi, Sphagnum majus*	James Bay lowland, Quebec, Canada	3 summer months with additional measurements in two winter months	Static closed chambers	
Rinne et al. (2007)	12.6	*Sphagnum balticum, Sphagnum majus*, *Sphagnum papillosum*, *Carex rostrata*, *Carex limosa*, *Eriophorum vaginatum*, *Scheuchzeria palustrus*	Siilaneva fen, Ruovesi, Finland.	12 months	Eddy covariance	From continuous monitoring, with some gap-filling using regression and linear interpolation

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Roulet et al. (1992)	1.746	Bogs: *Carex* spp., *Sphagnum* spp., shrubs, black spruce, tamarack	Canadian Low Boreal Wetlands	5.5 months	Static chambers	Area-weighted annually-integrated flux (only May – mid-November as all other times classed as zero flux)
	0.359	Fens: shrubs, graminoids and herbs				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Stamp (2011)	13.3 ± 1.6	Sedge lawns: *Sphagnum pulchrum*, *Erica tetralix*, *Myrica gale*	Cors Fochno, Wales	1 year	Static closed chambers	Time-integrated averages.
	14 ± 3	Mud-bottomed hollows: *Sphagnum cuspidatum, Menyanthes trifoliata*, *Rhynchospora alba, Eriophorum vaginatum*				
	9.9 ± 2.2	*Sphagnum* lawns: *Sphagnum pulchrum*, *Rhynchospora alba*, and *Eriophorum* spp.				
	5.9 ± 2.1	Hummocks: *Calluna vulgaris*, *Erica tetralix*, *Sphagnum capillifolium*				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Strack and Zuback (2013)	6.6	Natural: 90.3 % moss cover, 21.9 % vascular plant cover, 12.9 % shrub cover, 2.5 % sedge cover	Bois-des-Bel peatland, Quebec, Canada	5 months (May-Oct) with three winter measurements (Jan, Feb, Mar) on a subset of plots	Static closed chambers	Weighted values of mean fluxes based on spatial coverage of features where fluxes measured
	0.66	Unrestored: 0.1 % moss cover, 30.1 % vascular plant cover, 24.7 % shrub cover				
	0.68	Restored: 88.4 % moss cover, 20.3 % vascular plant cover, 10.8 % shrubs cover, 7.5 % sedge cover				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
Whalen and Reeburgh (1992)	1987: 0.47±0.16 1988: 4.38±1.35 1989: 4.78±1.56 1990: 0.54±0.12	*Aulucomnium* spp., *Hylocomium* spp., *Tomenthypnum* spp., *Polytrichum* spp.	Subarctic muskeg, permafrost underneath, seasonal active zone 0.5-1m.	4 years	Static chambers	Integration over time
	1987: 0.62±0.28 1988: 3.9±1.09 1989: 2.12±0.66 1990:	Intertussocks: Sparse cover by *Sphagnum* spp.				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)	Vegetation cover	Location	Duration of study	Flux measurement method	Annual flux calculation method
	0.79±0.36					
	1987: 4.88±0.73 1988: 0.81±1.09 1989: 4.27±0.67 1990: 60.6±8.66	*Carex aquatilis*				
	1987: 8.05±2.5 1988: 11.38±2.9 1989: 8.11±1.8	*Eriophorum vaginatum*				

Table 4.2: Approaches to annual CH_4 flux calculations

Reference	**Annual CH_4 flux ($g\ m^{-2}\ yr^{-1}$)**	**Vegetation cover**	**Location**	**Duration of study**	**Flux measurement method**	**Annual flux calculation method**
	1990 13.64±1.2					

4.2 Methods

4.2.1 Flux measurements

Fieldwork at each of the four study sites at Thorne and Hatfield Moors (Section 3.1) involved measuring both CO_2 and CH_4 fluxes using the static closed chamber method, as detailed in full in Section 3.2.2.2. In brief, CO_2 concentrations were measured directly within the chambers using an IRGA to collect data for both NEE (light chamber) and R_{TOT} (shrouded chamber). Measurements of PAR were taken using a handheld meter (Skye Instruments) before the NEE test inside each collar both with and without the chamber in place. In the end, the PAR data was not used due to the regular measurements of solar radiation data by the AWS; however, the PAR data did come in useful for examining the effects of the chamber material on incoming radiation values. During periods of cloud cover, the values were rarely different by more than a few µmol m^{-2} s^{-1}. Differences grew larger with increasing sunlight without cloud cover; however differences of more than 20 µmol m^{-2} s^{-1} were rare. Also, many times conditions were such that there would only be breaks of sunlight due to passing clouds in windy conditions, so the higher value of PAR was not always recorded inside or outside of the chamber. Therefore, any effects of the acrylic chamber on PAR were not considered to be an issue.

Samples of gas were collected from separate chamber tests to be analysed for their CH_4 concentrations via GC. Fluxes of both gases were calculated using the methods detailed in Section 3.2.2.3, based on Equation 3.3. Meteorological variables were recorded and downloaded from an AWS, and soil temperature and WTP were measured adjacent to each collar (Section 3.2.3) and later modelled (Section 4.2.2.2).

4.2.2 Annual flux calculations

4.2.2.1 Definition of an annual period

Fieldwork was conducted over 13 months from late September 2011 to late October 2012 , and so to calculate an annual total over 365 days, some of the data had to be excluded. Two separate calculations could have been made for each collar; the first starting from the earliest sampling date forwards until 365 days were included, and the second starting from the final sampling date backwards until 365 days were included. It was decided to choose the latter option. All of the collars and dipwells were installed in August 2011 and left to 'settle in' for a month before sampling. However, in mid-September the equipment at Site C was found to have been vandalised and had to be removed for repair. It was reinstalled in late September, only one day before sampling began. Therefore, in order to account for this disturbance, the first month of data was excluded, rather than the final month. Also, for the first few winter months of sampling, several of the dipwells at Sites C and D were empty. With the exclusion of this earlier data, the number of fluxes without associated WT data was reduced, leading to fewer assumptions during modelling. This decision affected the resulting annual CH_4 fluxes; if the earlier data had been included and the latter data was excluded, the differences in annual CH_4 fluxes would range from -2380.2 mg CH_4 m^{-2} to 1081.08 mg CH_4 m^{-2} depending on the collar in question.

4.2.2.2 Modelling annual carbon dioxide fluxes

Given the strong influence that solar radiation has on CO_2 fluxes, a modelling approach was needed in order to calculate annual fluxes. For the modelling described below, CO_2 fluxes were converted to units of mg CO_2 m^{-2} hr^{-1} to correspond with the hourly logging of the AWS (see Section 3.2.3.2).

The following environmental variables, recorded on an hourly basis by the AWS were used as model variables: air temperature, wind speed, barometric pressure,

rainfall, evapotranspiration and solar radiation. For CO_2 modelling, 24-hour totals of rainfall and evapotranspiration were used, rather than 'at point' values. Unfortunately, soil temperature and WTP were not continuously monitored, and so these two variables had to be modelled to provide hourly values. Soil temperature was modelled on a per-collar basis using linear regression in SPSS. Recorded soil temperature was tested against a range of recorded air temperatures and averaged air temperatures to find the best predictor. Air temperature averaged over the past 168 hours prior to the soil temperature measurement was found to be the best predictor for each of the 24 collars. All *p*-values were <0.001 and r^2 values ranged from 0.87 to 0.95. During subsequent modelling work the averaged air temperature over the previous 168 hours was used as a proxy for soil temperature due to the high r^2 values. Water-table position was modelled using a best subset non-linear multiple regression approach in Statistica (Version 10, StatSoft). The variables used were the WTP recorded on the previous field visit, the total rainfall over the 24 hours prior to the WTP measurement occurring, the total evapotranspiration over the same period, and a dummy variable to represent whether the recorded WTP was above or below the peat surface. All *p*-values werve <0.018 and r^2 values ranged from 0.5 to 0.97.

The approach chosen for CO_2 modelling was to use equations found in the literature. The P_G model from Tuittila et al. (1999) (Equation 2, as described in Section 4.1.2.1) was applied to the growing season of 2012. The growing season was defined through the construction of the ETI variable for the model. Following the guidance from Tuittila et al. (1999), the growing season was deemed to start when the 5-day moving-average air temperature was consistently >5 °C, which for the data collected at Thorne Moors was 01/05/2012, and continued through until the end of October 2012, after sampling had finished. Although the work by Tuittila et al. (1999) was conducted in Finland and not the UK, it was deemed that a 5-day moving average air temperature of 5 °C was still suitable for the UK climate to define the growing season by. Frich et al. (2002) also defined the growing

season starting point in the same way for a worldwide scale as an indicator for monitoring climate change.

The model was applied on a per-collar basis, and so the variable EV in Equation 2 was not needed. Also, the soil temperature measured during this study was at 9 cm depth, which changes the temperature variable used, and its symbol in the equation to T_{-9} There were two criteria to meet for the model to be accepted; the first was based on the direction of the resulting light response curve. The model was applied to data where the ETI and T_{-9} were constant, and solar radiation values were increasing. If the model produced a light response curve as shown in Figure 4.1, then the model was accepted. Models that produced light response curves that decreased with increasing solar radiation were rejected, because it is known that due to plant physiology, increased light intensity should result in increased P_G. Models also had to have an r^2 value > 0.4. Of the 18 collars (Site C excluded due to no vegetation cover) that the P_G model (Equation 2) was applied to, only five were accepted based on the criterion above. Therefore, the P_G model from Samaritani et al. (2011) (a variation of Equation 4.2) was tried on the remaining 13 collars. Equation 3 uses PAR instead of solar radiation; however, solar radiation was still used here because PAR was not recorded by the AWS. The same light response curve test was applied to the results of the Samaritani et al. (2011) P_G model as for the Tuittila et al. (1999) P_G model. A further three collars gained a successful P_G model from the application of Equation 3, resulting in a total of nine collars for which P_G could be modelled.

As Table 4.1 shows, a common approach to modelling R_{TOT} involves multiple linear regression using environmental variables such as soil temperature, WTP and air temperature. Both Tuittila et al. (1999) and Samaritani et al. (2011) modelled lnR_{TOT} using multiple linear regression. Tuittila et al. (1999) used WTP, soil temperature ETI and EV, whereas Samaritani et al. (2011) used soil temperature, WTP and air temperature. Both of these models were applied to the data from

Thorne and Hatfield Moors to see which gave the best fit; although, because the models were applied on a per-collar basis, EV was excluded from the Tuittila et al. (1999) model. The models were applied using SPSS, and stepwise multiple linear regression was used in every case because not all variables were returned as significant when all were entered together. Therefore, the majority of models only included one variable. Only models with an r^2 value > 0.4 were accepted. Overall 16 out of the 24 collars produced an accepted model for $R_{TOT.}$ Four models came from the Tuittila et al. (1999) model and three came from the Samaritani et al. (2011) model. For the remaining nine collars, both the Tuittila et al. (1999) and the Samaritani et al. (2011) stepwise models returned the same one variable and the same constant and coefficient values. If any models predicted values of P_G or R_{TOT} that were above the maximum values recorded during field measurements, then the models were capped to omit any data that exceeded the range of the model.

Only eight collars from three out of the four sites produced successful P_G and R_{TOT} models, and so these are the only collars for which annual NEE could be calculated. Therefore, a full comparison of NEE between the different sites and of any possible changes with time since restoration was not possible. The data from the eight collars with annual NEE results could only be used to provide an insight into the possible differences between sites.

4.2.2.3 Calculating annual methane fluxes, carbon dioxide equivalents and global warming potential

Table 4.2 highlights that there are many different methods used to calculate annual CH_4 fluxes, unlike the very similar methods shown in Table 4.1 for modelling annual CO_2 fluxes. Unlike many of the studies in Table 4.2, this study included chamber flux measurements conducted in the winter months, as well as a more intensive regime over the summer months, as described in Section 3.2.1.

As described in Section 3.2.2.3, CH_4 fluxes were calculated for each collar on each field visit, in units of mg CH_4 m^{-2} day^{-1}. In order to produce an annual methane flux for each collar, and therefore each of the four study sites, the following approach was adopted. It was assumed between one field visit and the next that the CH_4 flux did not change, and so a weighted total was calculated for each collar to give an annual flux. For example, the flux measured on 02/08/2012 was applied to each subsequent day until the next flux measurement on 16/08/2012. This new flux was then applied to the subsequent days until the next flux measurement, and so on. If a flux measurement was conducted, but the resulting flux could not be accepted, then the previous accepted flux was assumed to still apply until the next accepted flux. For each collar this resulted in 365 daily fluxes, which were summed together to make an annual flux (mg CH_4 m^{-2}). Although previous statements advocate the use of models to better predict CH_4 fluxes in comparison to false assumptions that CH_4 emissions would remain stable between sampling dates, time constraints prevented any attempts to model the CH_4 flux data, as with the CO_2 flux data. A multiple liner regression modelling approach using all of the associated environmental and meteorological data collected alongside the CH_4 flux data could have been used to try and find predictors of CH_4 fluxes, as with the CO_2 R_{TOT} models detailed in Section 4.2.2.2. Such a modelling approach, if successful would have provided a more accurate estimation of CH_4 fluxes in the time periods between chamber flux measurement tests. Dinsmore et al. 2010 used a best subset regression approach when modelling aquatic CH_4 evasion, and Wilson et al. 2013 employed a multiple non-linear regression model for CH_4 fluxes; therefore, if multiple linear regression did not provide satisfactory results, other options would have been available.

The annual CH_4 flux totals were also converted into CO_2-e to be able to compare them against annual NEE totals and calculate GWP for the collars that had a fully modelled annual CO_2 budget. The current IPCC estimate for the GWP of CH_4 on a 100-year timescale is 28 (Myhre et al., 2013). Therefore, the annual CH_4 fluxes can be converted to CO_2-e on a 100-year timescale by multiplying the CH_4 fluxes by 28

(Baird et al., 2009). The values of CO_2-e were then added to the NEE to produce values of GWP for each collar where NEE was successfully modelled.

4.2.3 Seasonal flux calculations

Seasonal fluxes were calculated by splitting the annual fluxes for both CO_2 and CH_4 into seasons. There were only two seasons included in the seasonal flux calculations; summer and winter. Winter was defined to be from the start of the annual flux calculations for each site (late October 2011) through until the start of fortnightly fieldwork (early April 2012). Summer was defined to be from early April 2012 through until the end of the measurement campaign (late October 2012). Winter CO_2 fluxes only include R_{TOT} calculations, because P_G was only modelled during the growing season (from May 2012 onwards).

4.2.4 Statistical analyses

Analysis of variance (ANOVA) was used to test for significant differences between annual CH_4 fluxes on a per-site basis. Paired *t*-tests were used to determine if winter and summer fluxes of both CH_4 and CO_2 (NEE) were statistically different at each site, on a per-site basis. Multiple linear regression was used to determine the drivers of CH_4 fluxes on a per-site basis. Variables used included air temperature, barometric pressure and wind speed at the time the test was being conducted and averages of the previous 72 and 168 hours (and 24 hours for wind speed); total rainfall in the previous 24, 72 and 168 hours; WTP at the time the test was being conducted and the change since the previous test; solar radiation 'at test' and totals over the previous 24, 72 and 168 hours; vegetation cover; and peat depth. Peat depths were measured adjacent to each collar using a dutch auger, with one measurement per collar. Vegetation cover was assessed from photographs of each collar on a presence/absence basis. Three photographs were used per collar from mid-October 2011, late July/early August 2012 and late October 2012 to represent the start and end of sampling and the peak time of CH_4 fluxes, and the times in between the photographs were assumed to be the same. A 100-square grid was

placed over each photograph, and within each square if a vegetation type was present, it was assigned a value of one. Therefore, if a vegetation type was present in 50 out of 100 squares, it received a value of 50. These totals were taken forward into the multiple regression analyses. The variables returned by the multiple regression model were only accepted as driving variables if they were significant ($p < 0.05$); and if the overall model was significant, had an r^2 value > 0.4 and the tolerance (a measure of collinearity between the variables) was > 0.4. All statistical analyses were performed using SPSS.

4.3 Results

4.3.1 Environmental and meteorological variables

Figures 4.2, 4.3 and 4.4 show the environmental and meteorological variables recorded alongside gaseous flux sampling over 13-months. Water-table positions (Figure 4.2) and soil temperature (Figure 4.3) were measured as described in Section 3.2.4.1. The meteorological variables in Figure 4.4 were measured as detailed in Section 3.2.4.2.

The WTPs at Sites A and B were much higher than at Sites C and D. The original aim had been for the WTPs at Sites A, B and D to be similar; however, a dry summer combined with the underlying mineral substrate at Site D consisting of sand unfortunately prevented this. From December 2011 at Site A, and from February 2012 at Site B, the WTP at some, if not all collars was above the peat surface for the rest of the sampling period. Although there was generally a rise in WTP at Sites C and D as the sampling period progressed, the WTP was below the peat surface for all the sampling period. There were two exceptions at Site C on 17/07/2012 where the WTP at collar C1 was level with the peat surface and at collar C2 was 31 mm above the peat surface. Many of the collars at Sites C and D had a WTP more than 200 mm below the peat surface for the vast majority of the sampling period.

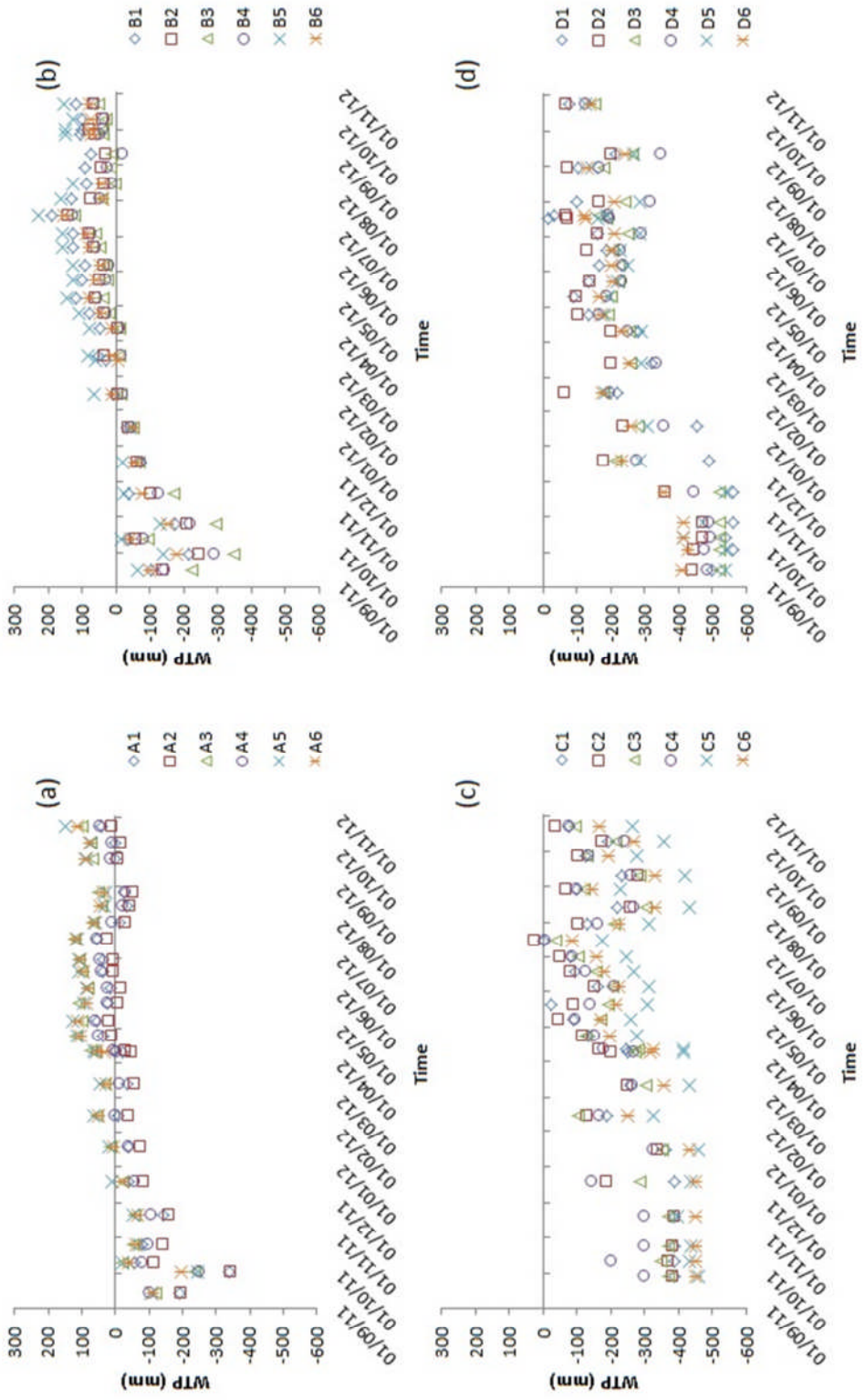

Figure 4.2: Water-table position measured on each sampling occasion at (a) Site A, (b) Site B, (c) Site C, (d) Site D. The x-axis represents the peat surface; therefore, positive values represent surface inundation and negative values represent depth below the peat surface.

At all sites the average soil temperature for the six collars per site followed the same pattern over the 13-month sampling period, as shown in Figure 4.3. The lowest soil temperatures were recorded in January 2012 at all sites, except for Site B where the lowest soil temperature was recorded in February 2012. The warmest soil temperatures were recorded at different times of year depending on the site in question. For Site A the warmest soil temperature was recorded in June 2012, in July 2012 at Sites B and D, and in August 2012 at Site C.

The data for both the air temperature and solar radiation values shown in Figure 4.4 follow a seasonal pattern. There were higher rainfall totals over the summer and autumn of 2012 compared with the previous spring and winter, as reflected in the WTP data in Figure 4.2.

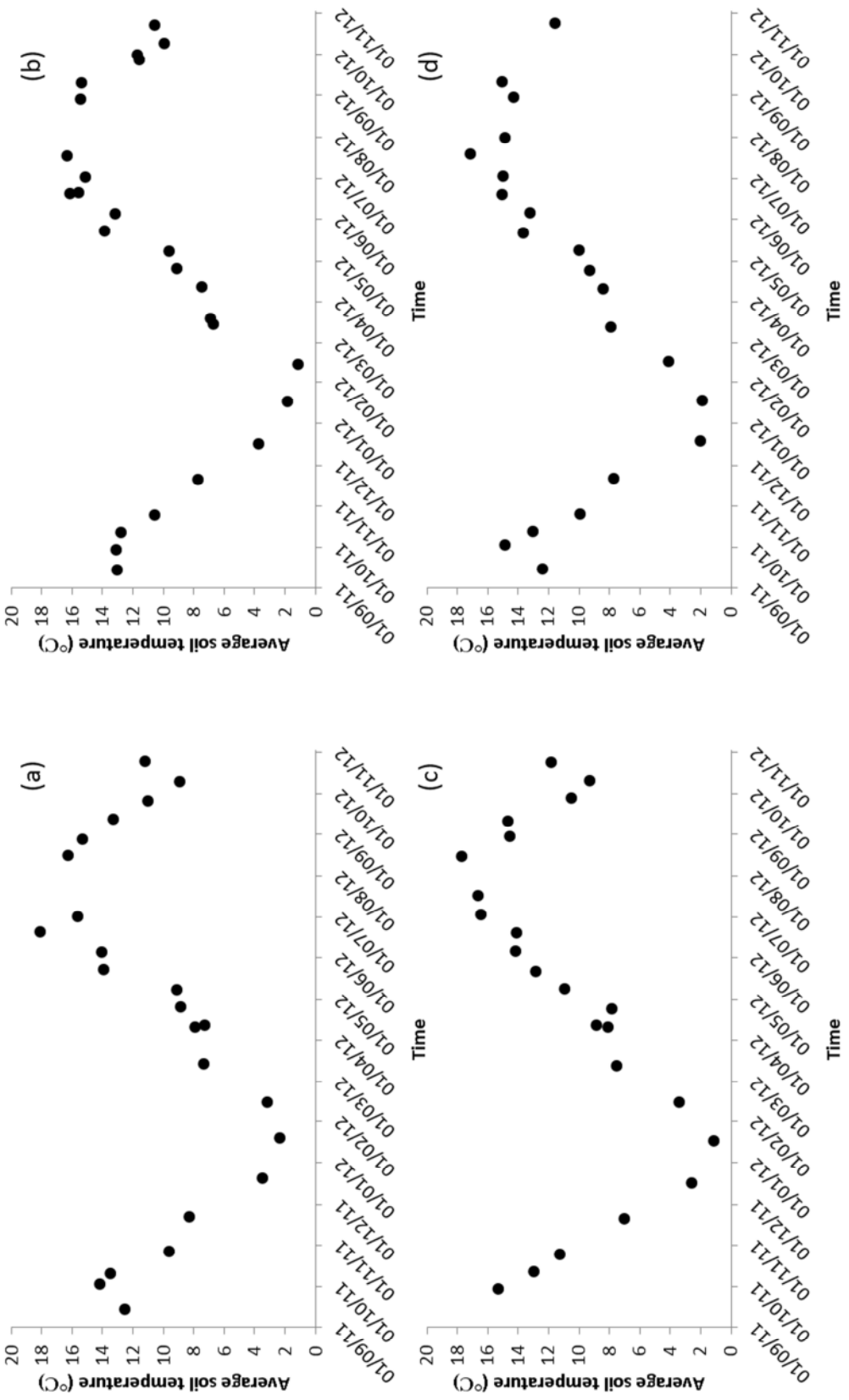

Figure 4.3: Average soil temperature from the six collars on each sampling occasion at (a) Site A, (b) Site B, (c) Site C and (d) Site D

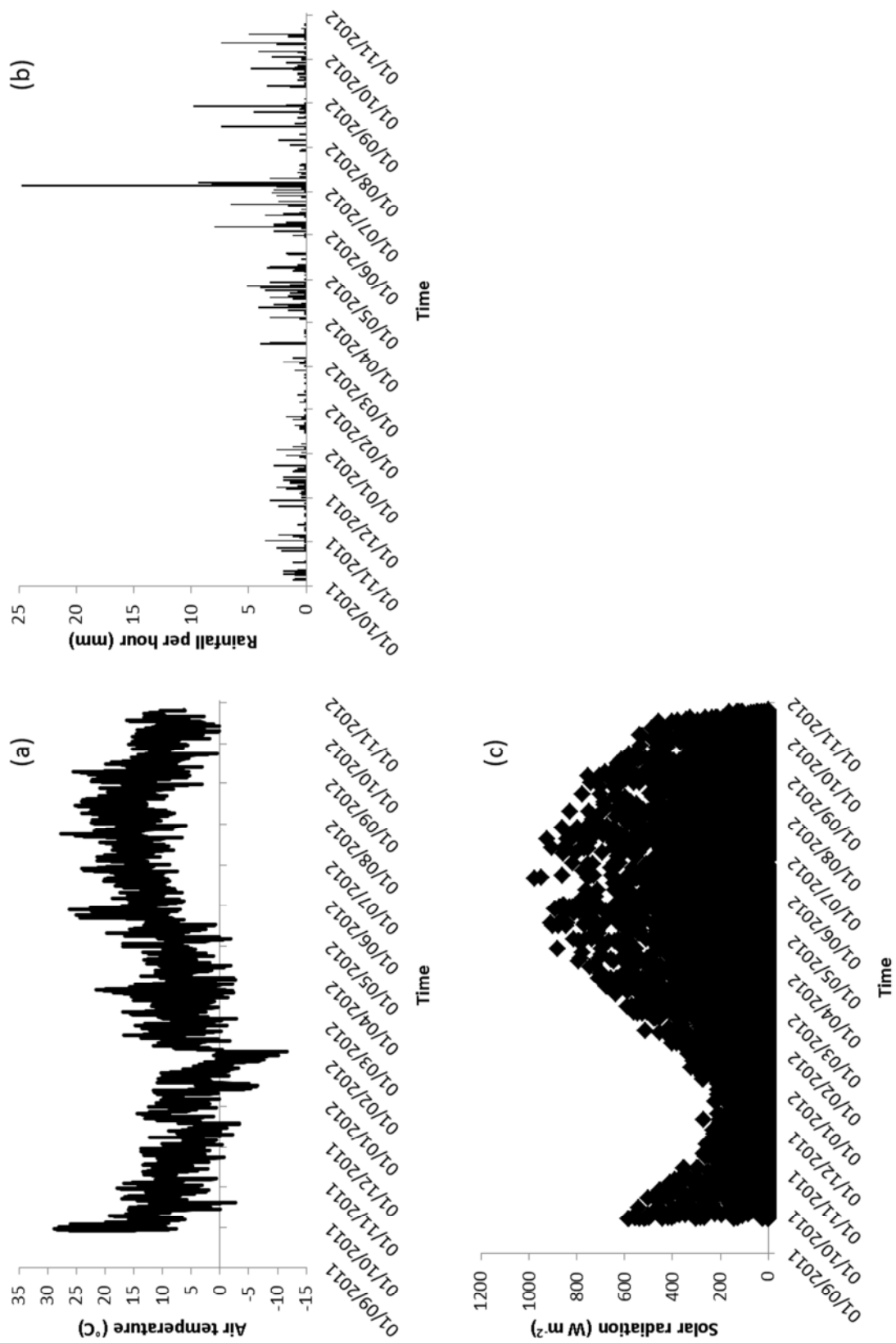

Figure 4.4: Meteorological variables recorded at Thorne Moors: (a) air temperature; (b) rainfall; (c) solar radiation

4.3.2 Measured gaseous fluxes and their drivers

4.3.2.1 Measured methane fluxes

Figure 4.5 shows the CH_4 fluxes measured during each site visit for each collar. When gaseous flux sampling started in late September/early October 2011, the air temperatures were unusually warm reaching up to 28.9 °C on 30/09/2011, as shown in Figure 4.4a. The effects of these high temperatures are reflected in the initial CH_4 fluxes recorded at all four sites, as shown in Figure 4.5. Due to the choices made in defining a 365 day period for annual flux calculations (Section 4.2.2.1), these initial high CH_4 fluxes were not included in the annual CH_4 flux calculations. At Site A in early October 2011 there was a high negative CH_4 flux at collar A4; an occurrence that was never measured again at that or any other collar. There were some very small negative CH_4 fluxes measured on one occasion at collar C5 (-2.88 mg CH_4 m^{-2} day^{-1}) and on three occasions at Site D (ranging from -1.55 to -4.12 mg CH_4 m^{-2} day^{-1} at collar D5 and -1.81 mg CH_4 m^{-2} day^{-1} at collar D4). All of the negative fluxes at Sites C and D were included in the annual flux calculation period.

Throughout the winter months the fluxes at Sites A and B only rarely rose above 30 mg CH_4 m^{-2} day^{-1}, and at Sites C and D the fluxes rarely rose above 10 mg CH_4 m^{-2} day^{-1}. From April 2012 the fluxes at Sites A and B begin to rise, each reaching a peak in early August 2012 before starting to decline. At Sites C and D there is no rise throughout the growing season, with the exception of collar D3, which contained a small tussock of *Eriophorum vaginatum*. These differences between the sites and the difference between collar D3 and remaining five collars at Site D highlight the influence that vascular plant cover appears to have on CH_4 fluxes. The pattern of the fluxes from collar D3 compared with collars from Sites A and B which have *E. vaginatum* cover (A1, A4, B4, B6) shows the difference between emergent and more mature plants of the same species. The fluxes from collar D3 continue to rise throughout the entirety of the growing season, whereas at Sites A and B, fluxes from all of the collars reach a peak and start to decline before the end of the

growing season. However, there was only one collar containing emergent *Eriophorum*, and therefore it is not possible to draw wider conclusions from this difference. The larger variation in fluxes at Sites C and D in winter compared to summer is also highlighted in Figure 4.5.

4.3.2.2 Drivers of methane fluxes

Multiple linear regression was used to identify the drivers of CH_4 fluxes on a per-site basis and Table 4.3 shows the results. Some of the results indicate that individual collars have strong influences on the results of a site as a whole. At Site A, bare peat cover was returned as a significant variable, yet it was only present within collar A2 during the winter months. During these winter months, the CH_4 flux from collar A2 was a zero flux for every accepted flux measurement, as shown in Figure 4.5a. Similarly, the amount of *Sphagnum cuspidatum* cover was a significant variable for Site B, but it was only visible in the photographs of collar B3, and only during the summer months, which is when the CH_4 fluxes from collar B3 began to rise (see Section 4.2.4 for details on vegetation cover analysis). An increase in *Sphagnum cuspidatum* cover would be expected to cause a reduction in CH_4 fluxes due to the presence of methanotrophs living within the hyaline cells (Raghoebarsing et al., 2005). *Eriophorum vaginatum* was only present in collar D3 at Site D, and yet was one of only two variables returned by the multiple regression analysis for Site D.

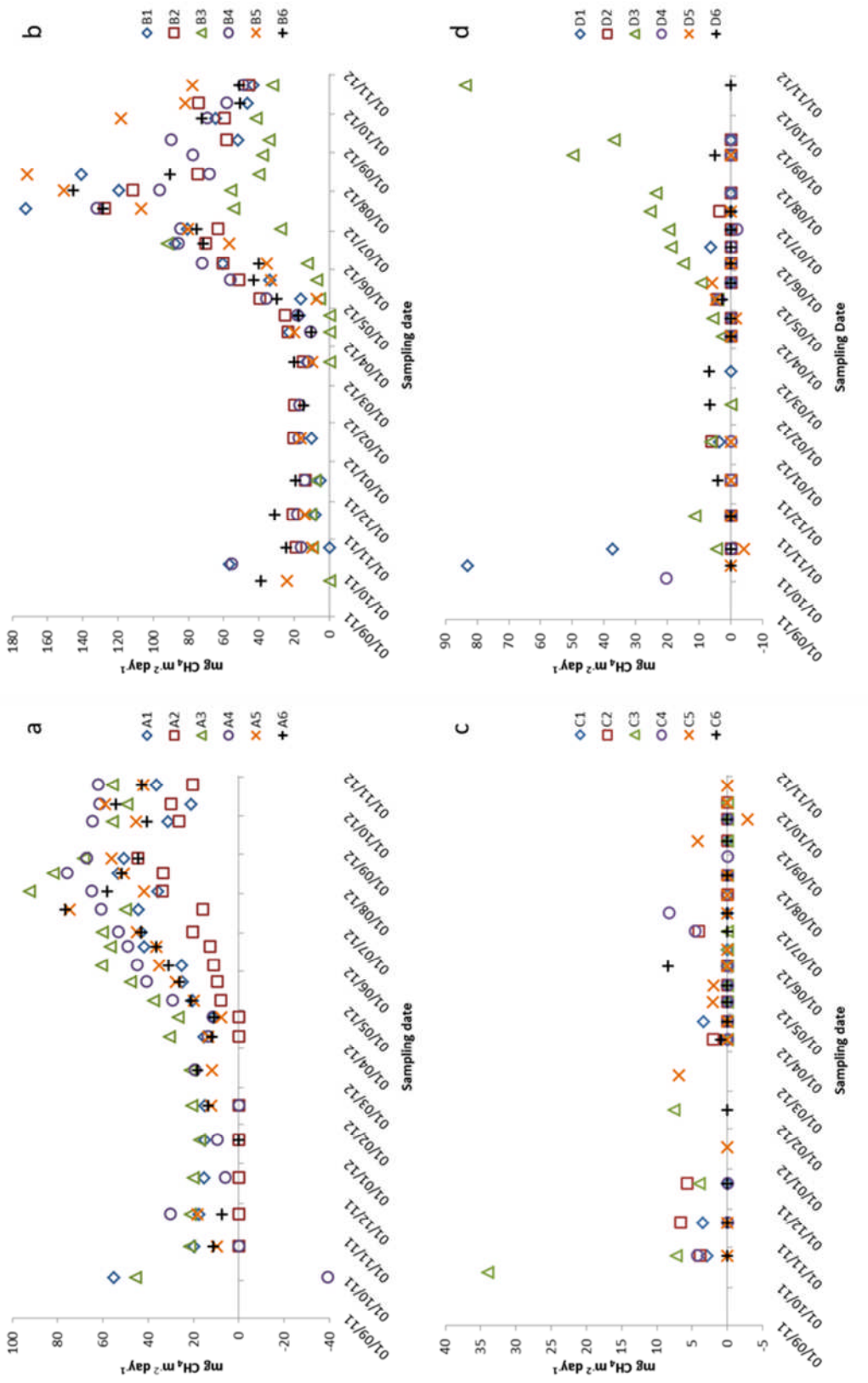

Figure 4.5: Methane fluxes on a per-collar basis for the 13-month sampling period for: (a) Site A; (b) Site B; (c) Site C and (d) Site D

Table 4.3: Drivers of CH_4 fluxes per-site as defined by multiple linear regression

Site	r^2	*n*	CH_4 flux drivers
A	0.72	100	Average air temperature over previous 168 hours Amount of bare peat cover Average wind speed over previous 168 hours WTP during test Peat depth
B	0.67	102	WTP during test Average air temperature over previous 72 hours Cumulative solar radiation over previous 72 hours Amount of *Eriophorum angustifolium* cover Amount of *Sphagnum cuspidatum* cover
C	0.52	74	Average wind speed over previous 168 hours Average barometric pressure over previous 72 hours Average wind speed over previous 24 hours Cumulative solar radiation over previous 72 hours Average air temperature over previous 168 hours Cumulative rainfall over previous 24 hours Peat depth
D	0.45	77	Amount of *Eriophorum vaginatum* cover Average wind speed over previous 24 hours

4.3.2.3 Measured carbon dioxide fluxes

The measured carbon dioxide fluxes over the 13-month sampling period are shown in Figures 4.6 (NEE) and 4.7 (R_{TOT}). During the winter months, the NEE values at Sites A, B and C are mostly positive (CO_2 release to the atmosphere); however, at Site D the winter NEE values are mostly negative (CO_2 uptake from the atmosphere). At Site C there was one high positive NEE value (16711 mg CO_2 m^{-2} day^{-1}) at collar C2, accompanied by a high R_{TOT} value (21776 mg CO_2 m^{-2} day^{-1}). On this date the peat had frozen, and this was the only sampling date where frozen peat was encountered. However, the NEE and R_{TOT} fluxes recorded at collars C4 and C5 on this date were similar to the previous and following sampling dates. During the spring, summer and autumn months, the NEE values at all four sites become more varied. At Site A the largest variation was on 16/08/2012 at 36029 mg CO_2 m^{-2} day^{-1}. At Site B on 20/06/2012 the variation was 41620 mg CO_2 m^{-2} day^{-1}. The largest variation at Site D was on 19/07/2012 at 27764 mg CO_2 m^{-2} day^{-1}. If the sampling date at Site C where the peat was frozen is discounted, then the largest variation was on 31/07/2012 at 8575 mg CO_2 m^{-2} day^{-1}. Two collars at Site D (D3 and D4) showed increasingly negative NEE values (increasing CO_2 uptake) as the summer months progressed. Collar D3 contained a small tussock of *E. vaginatum* and collar D4 contained *S. cuspidatum* and more *C. vulgaris* than any of the other collars. With the exclusion of winter fluxes at Site D, there were only two sampling dates at Site C, three at Sites B and D and four at Site A where all NEE values measured were negative.

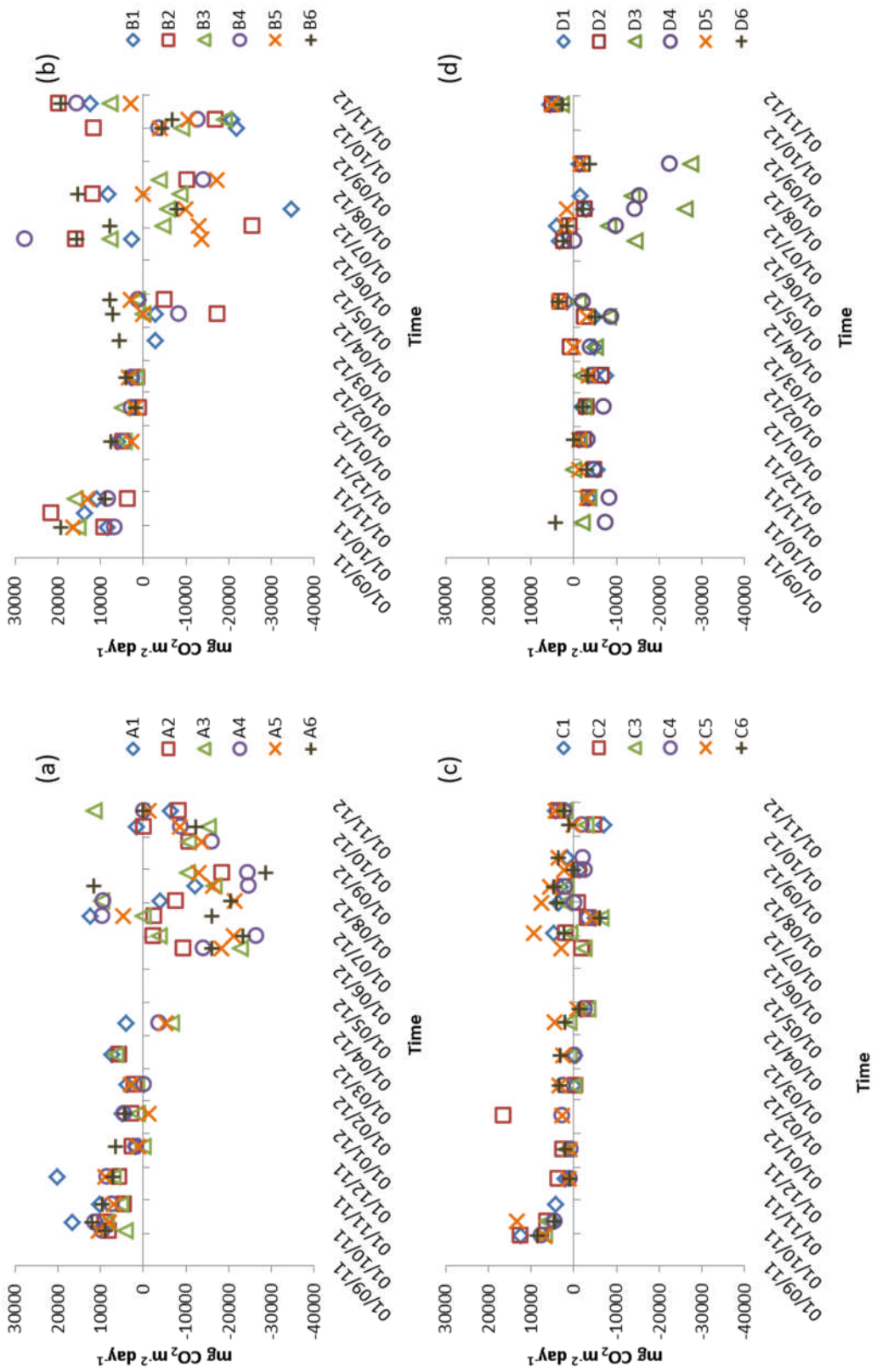

Figure 4.6: NEE fluxes on a per-collar basis for the 13-month sampling period for (a) Site A, (b) Site B, (c) Site C and (d) Site D. Negative values indicate uptake from the atmosphere, positive values indicate release to the atmosphere.

At all sites, the R_{TOT} values decline from the first autumn months into the winter; however, the rise in these values during the following spring and summer months is much more pronounced at Sites A and B than at C and D. From June 2012 onwards the variation in R_{TOT} values measured during each sampling visit at Sites A and B show a marked increase. For example, at Site B on 25/04/2012 the range of measured R_{TOT} values is 3838 mg CO_2 m^{-2} day^{-1}, whereas on 20/06/2012 this range increases to 29315 mg CO_2 m^{-2} day^{-1}. For the entire sampling period the majority of the RTOT values measured at Sites C and D are below 10000 mg CO_2 m^{-2} day^{-1}. Yet, at Sites A and B it is only the majority of the winter values that are below 10000 mg CO_2 m^{-2} day^{-1}.

4.3.2.4 Drivers of carbon dioxide fluxes

The drivers of CO_2 fluxes were only assessed through the results of modelling P_G and R_{TOT}; no further analyses were conducted. Table 4.4 shows that soil temperature was a strong predictor of R_{TOT} for collars at Sites A and B, and WTP became an additional predictive variable for collars at Site C. The variables WTP, ETI and air temperature (depending on which model was used) were all available for input into the R_{TOT} models. However, with the exception of WTP for collars C3 and C6, none of these variables were accepted for inclusion into the stepwise regression models for any of the collars in Table 4.4, which indicates that they did not add any further predictive value to the model after soil temperature was included. For P_G, solar radiation and WTP were strong predictors, with ETI as an additional variable for collar A2, and air temperature as an additional variable for collars A5, A6 and B1.

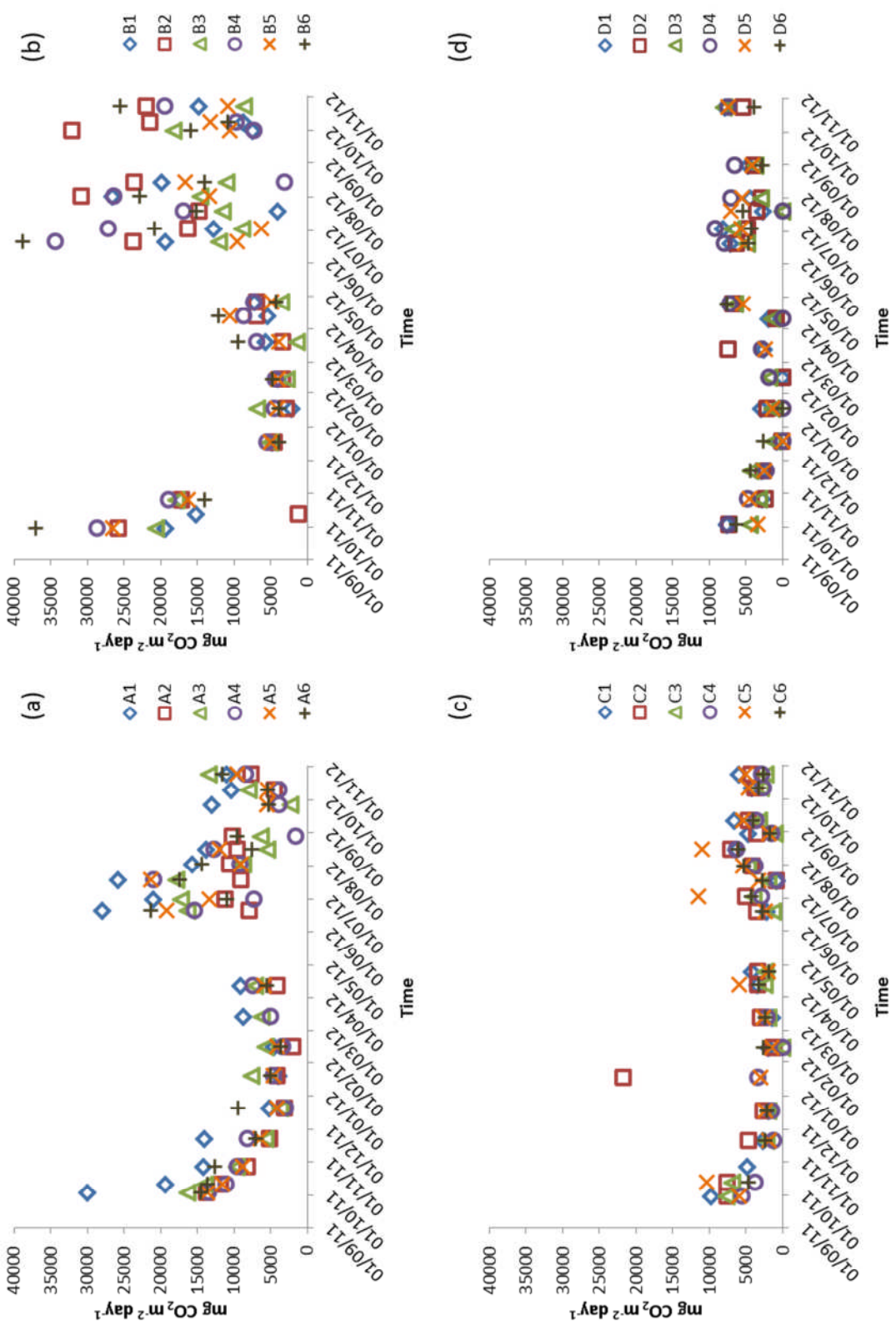

Figure 4.7: R_{TOT} fluxes on a per-collar basis for the 13-month sampling period for (a) Site A, (b) Site B, (c) Site C and (d) Site D

4.3.3 Annual fluxes

4.3.3.1 Annual net ecosystem exchange

Table 4.4 shows the NEE values for the six collars which produced successful P_G and R_{TOT} models. For all of the collars for which NEE could be calculated, there was a net loss of CO_2 to the atmosphere. The smallest loss of 346.5 g CO_2 m^{-2} was from collar A6, which had the highest P_G at -2801.4 g CO_2 m^{-2}. The highest loss of 1415.2 g CO_2 m^{-2} was from collar A2, which had the smallest P_G at -1254.9 g CO_2 m^{-2}. Both of these collars were located at Site A, which highlights the variability in NEE that can be found on one site. The R_{TOT} for collar C3 was capped at 300 mg CO_2 m^{-2} hr^{-1} because the highest R_{TOT} field measurement was 281 mg CO_2 m^{-2} hr^{-1}, yet the model predicted peaks up to almost 600 mg CO_2 m^{-2} hr^{-1}, and was deemed to be unreliable. There were no possible NEE calculations for Site D, and only one for Site B, so it is not possible to draw clear comparisons between sites for NEE.

Figure 4.8 shows the distribution of P_G and R_{TOT} for the collars in Table 4.4, modelled on an hourly basis. The pattern within the R_{TOT} models for collars A2, A5, A6 and B1 are very similar, because they are all derived from soil temperatures. The R_{TOT} for collars C3 and C6 are derived from both soil temperature and WTP; hence, the more varied distribution. In all cases, R_{TOT} begins to increase with the onset of the growing season, and is at its lowest in February 2012. The P_G models for collars A5, A6 and B1 were both based on the same variables, yet have slightly different distributions. For collar B1 there is a clear peak in late July 2012, whereas for collar A6 the peak is not as well defined, and is earlier in late May 2012.

Table 4.4: Net ecosystem CO_2 exchange (g m^{-2}) for an annual period from late October 2011 until late October 2012. Negative values indicate uptake from the atmosphere, positive values indicate release into the atmosphere. Models were from Tuittila et al. (1999) (Tu) and Samaritani et al. (2011) (Sa). Tu/Sa indicates that the results of both models were identical.

Collar	P_G	**Variables**	**Model**	r^2	R_{TOT}	**Variables**	**Model**	r^2	**NEE**
A2	-1254.9	Solar radiation, *ETI* and soil temperature	Tu	0.73	2679.1	Soil temperature	Tu/Sa	0.84	**1415.2**
A5	-2233.7	Solar radiation, *WTP* and air temperature	Sa	0.85	3402			0.73	**1168.2**
A6	-2801.4			0.88	3147.8			0.42	**346.5**
B1	-2648.7			0.97	3550			0.51	**900.5**
C3	N/A				706.5	Soil temperature and WTP		0.6	**706.5**
C6					1160.7			0.56	**1160.7**

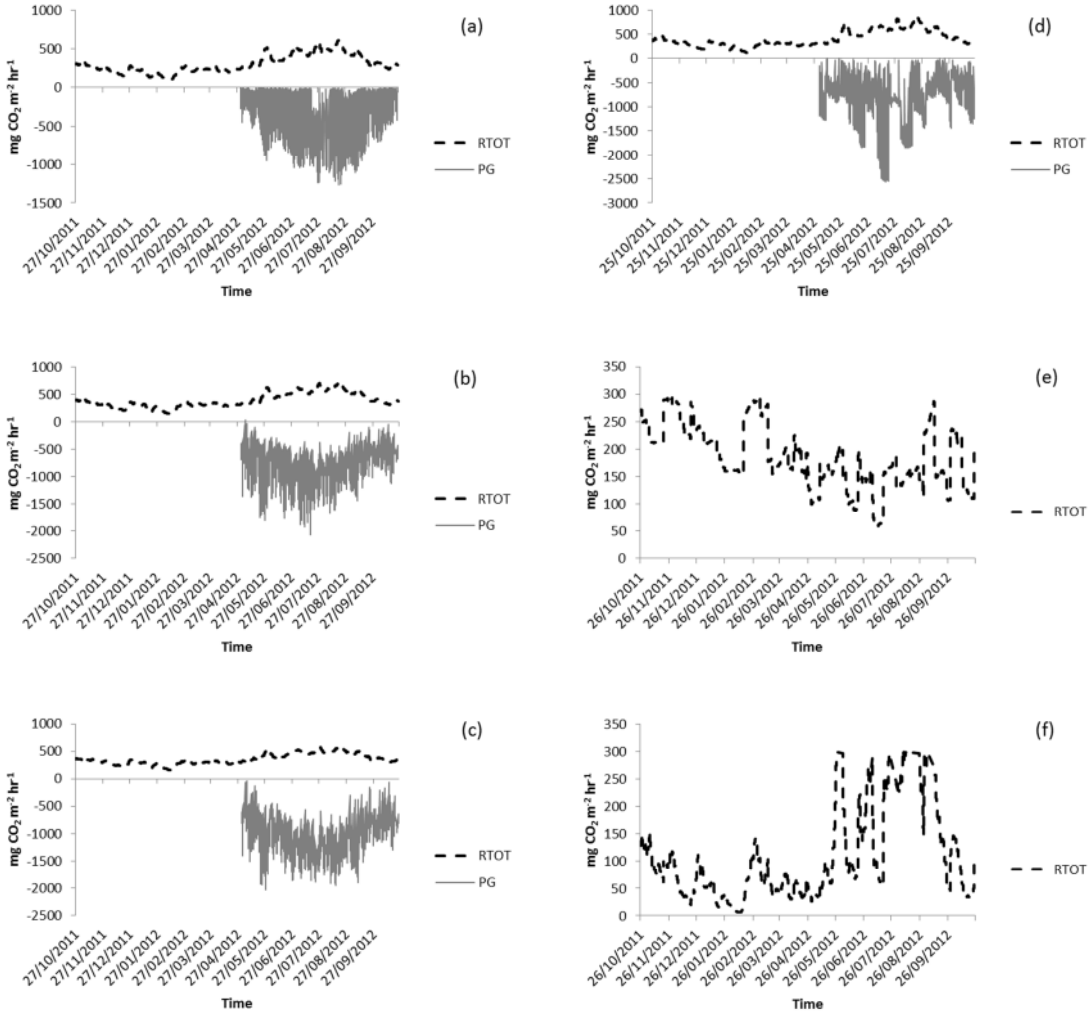

Figure 4.8: Division of NEE into P_G and R_{TOT} : (a) A2; (b) A5; (c) A6; (d) B1; (e) C3; (f) C6. Note the differences in the axis scales.

4.3.3.2 Annual methane fluxes and carbon-dioxide equivalents

Figure 4.9 shows the annual CH_4 fluxes, as calculated using a weighted-total approach, for each site. The highest annual flux totals were recorded on Site B (19476 mg CH_4 m^{-2}), which also had the largest range of fluxes. Site C had the smallest range of fluxes, but the lowest annual flux total for a collar was recorded at Site D, with a negligible CH_4 uptake of -0.11 mg m^{-2}. There were significant differences between the fluxes from the four different sites (ANOVA, p <0.001). A Tukey post-hoc test showed that the fluxes from Site C and Site D were not significantly different to each other (p = 0.959). Sites A and B had significantly different fluxes from each other (p = 0.022). All other site combinations also had significantly different fluxes (p < 0.001). Table 4.4 shows the annual CH_4 flux totals per site, and the same totals converted to CO_2-e.

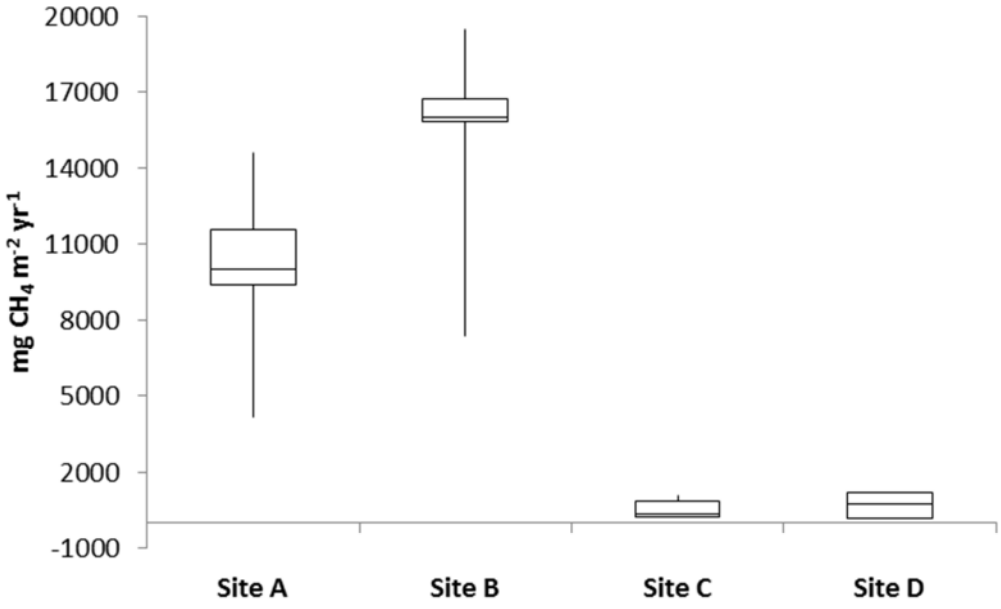

Figure 4.9: Annual CH_4 fluxes per site. Boxplot convention is as follows: boxes indicate the interquartile range; the central line through each box indicates the median; the far extent of the upper and lower lines extending from each box indicate the maximum and minimum.

Table 4.5: Annual CH_4 and CO_2-e fluxes per site

Site	g CH_4 m^{-2}	g CO_2-e m^{-2}
A	60	1681
B	91.7	2567
C	3.31	92.7
D	8.25	231

4.3.3.3 Global warming potential

The totals of NEE for the six collars shown in Table 4.4 and the respective totals for CO_2-e were added together to calculate the GWP on a per-collar basis, as shown in Table 4.6. As with NEE, the three collars at Site A produced both the highest and lowest GWP of the six collars overall. The one collar from Site B produced a higher GWP than either of the collars from Site C. However, due to there only being results for six collars out of a possible 24, there is not enough data to draw any definitive conclusions about differences between sites and possible reasons for these differences.

Table 4.6: Global warming potential on a per-collar basis. All values in g CO_2/CO_2-e m^{-2}. Positive values indicate release to the atmosphere

Collar	NEE	CO_2-e	GWP
A2	1415.2	116.8	**1532**
A5	1168.2	297	**1465.2**
A6	346.5	264.2	**610.7**
B1	900.5	445.7	**1346.2**
C3	706.5	30.6	**737.1**
C6	1160.7	29.3	**1190**

4.3.4 Seasonal fluxes

4.3.4.1 Seasonal carbon dioxide fluxes

Figure 4.10 shows the winter and summer totals of NEE on a per-collar basis. As Table 4.4 shows, all collars had a positive annual NEE, but Figure 4.4 shows that collars A6 and B1 were the only collars where NEE was negative during the summer months. For the remaining collars, winter NEE totals were greater than summer totals, showing the effects of P_G on the summer totals, with the exception of collars C2 and C3 where there was no P_G. For collar C2, NEE was higher in winter, whereas for collar C3 the opposite was observed.

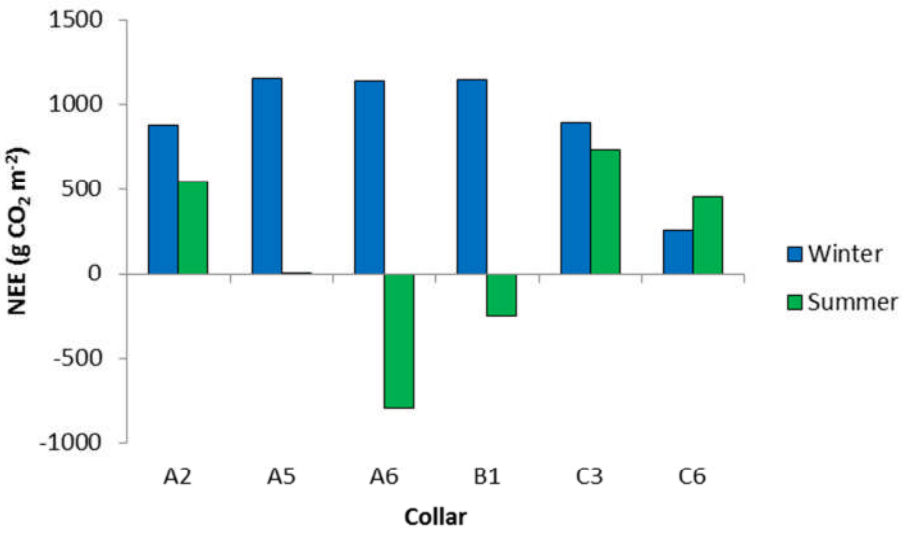

Figure 4.10: Seasonal NEE totals per collar. A5 summer flux = 9.53 g CO_2 m^{-2}. Positive values indicate release to the atmosphere, negative values indicate uptake

4.3.4.2 Seasonal methane fluxes

Figure 4.11 shows the winter and summer fluxes of annual CH_4 fluxes on a per-site basis. For Sites A and B summer fluxes were significantly greater ($p < 0.001$) than winter fluxes, whereas at Sites C and D fluxes were not significantly different between seasons. The range in CH_4 fluxes at Sites A and B was larger in the summer than the winter. However, for Sites C and D, a larger range in fluxes was

observed in the winter than the summer, with the exception of one collar at Site D which produces the outlier. This outlier is from collar D3, which contained a small tussock of *Eriophorum vaginatum*, and produced increasingly larger CH_4 fluxes as the growing season progressed. These differences in the magnitudes of summer and winter fluxes suggest that the drivers of CH_4 fluxes at Sites A and B become more prevalent in the summer months, whereas the drivers of CH_4 fluxes at Sites C and D are more prevalent in the winter months.

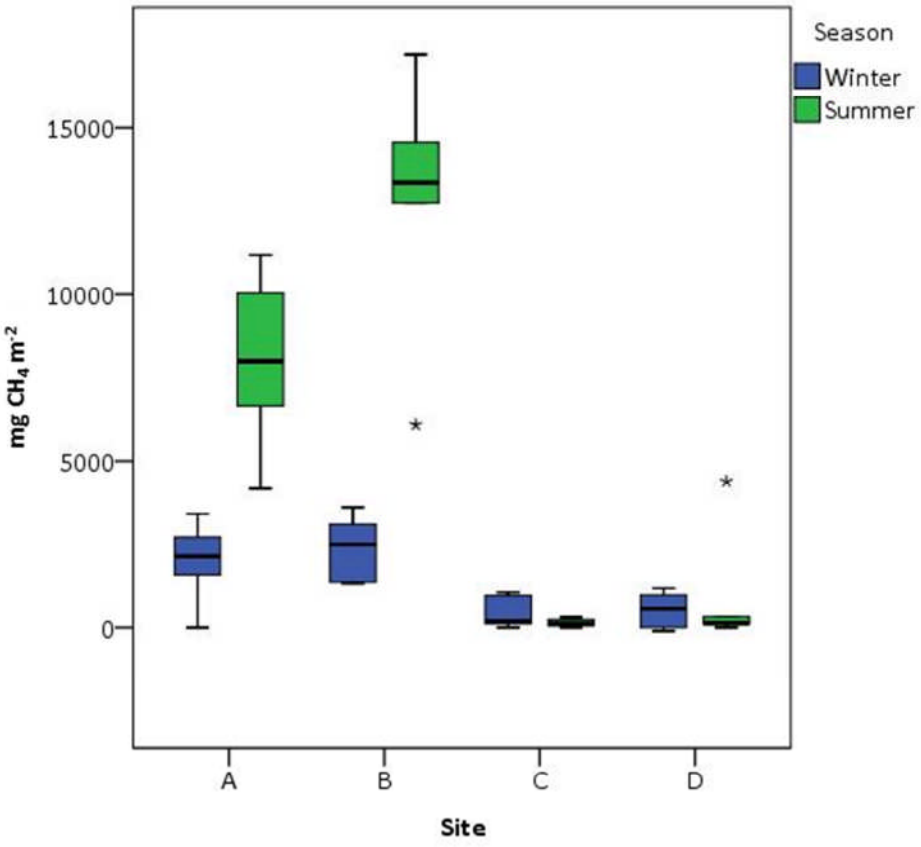

Figure 4.11: Seasonal distribution of annual CH_4 fluxes per site. Boxplot convention is as for Figure 4.3, except for where an asterisk replaces the maximum or minimum value. An asterisk represents an outlier > three times the interquartile range. *n* = 6 per site.

4.4 Discussion

4.4.1 Global warming potential and implications for peatland restoration

All of the six collars for which NEE could be calculated were net emitters of CO_2 to the atmosphere, regardless of time since restoration started. With the CH_4 emissions converted to CO_2-e and added to the NEE totals, the overall GWP for each of the six collars were also all positive, indicating a net warming effect on the atmosphere. Site C was the control site, with no vegetation cover, and a low WTP; however, the total NEE from collars C2 and C3 was 1867.2 g CO_2 m^{-2}, an average of 933.6 g CO_2 m^{-2} per collar. From the four collars from Sites A and B combined the total NEE was 3830.4 g CO_2 m^{-2}; an average of 957.6 g CO_2 m^{-2} per collar. Therefore, there are no obvious effects of restoration within the NEE totals from these six collars; in fact, on average, the collars in the restored areas are losing more CO_2 to the atmosphere than those where restoration has yet to occur. These NEE totals have a strong effect on the resulting GWP values, which follow the same pattern per collar as the NEE totals (Table 4.5). The year in which this study occurred had a higher-than-average rainfall total (see Section 3.1.3), and was the wettest year on record between 1992 and 2012. However, it is unknown if this increased rainfall had an effect on the gaseous fluxes; although, WTP was returned as a CH_4 flux driver for Sites A and B (Table 4.3), and WTP was also included in the P_G models for collars A5, A6 and B1, and in the R_{TOT} models for collars C3 and C6 (Table 4.4). In terms of differences between Sites A and B, the WTP at Site B was generally higher (deeper surface inundation for the summer months), and the *Eriophorum* plants at Site B were also more robust. From a land-management perspective, in terms of carbon storage, restoration has not had the desired effect for these four collars from Sites A and B. However, due to the small size of the available data, no overall conclusions can be drawn as yet.

The hypothesis presented by Bain *et al.* (2011) (Figure 2.4) indicated that within the first ten years following restoration, the GWP should still be positive, but much lower than pre-restoration values. No evidence for this predicted change can be seen in the results presented in this chapter. Of the three phases of restoration presented by Joosten *et al.* (2006) (Figure 2.3), phase 1 showed an overall increase in GWP following restoration. The best-case scenario for phase 1 was that it would only last for five years (Joosten *et al.* 2006). It is more than five years since restoration started at both Sites A and B, which indicates that this scenario is not valid for Thorne Moors. In the worst-case scenario, phase 1 lasts for 50 years (Joosten *et al.* 2006); however, restoration has not been ongoing at Thorne Moors for that time period yet.

The low WTP at Site D was not what might be expected for a peatland four years after restoration started; especially during the wettest year on record for the area since 1992. As Table 3.1 shows, the mineral substrate beneath Site D is sand; therefore, despite the high rainfall it was still difficult for land managers to maintain a high and stable WTP for peatland restoration. Comparisons of this study with the hypotheses of Joosten et al. (2006) and Bain et al. (2011) are limited. Joosten et al. (2006) suggested that the GWP of a recently restored site would be significantly higher than sites where restoration had been ongoing for nine and 15 years. The hypothesis presented by Bain et al. (2011) indicated that, post-restoration, the GWP of a UK peatland would be lower than when the area was being drained. The conditions at Site D were unrepresentative of a restored peatland, and there were no acceptable NEE calculation for any of the collars. Therefore, it is unclear as to whether the predicted post-restoration spike in GWP from the Joosten et al. (2006) hypothesis would have been evident if the WTP at Site D had been closer to the assumed desired level near the peatland surface. Bain et al. (2011) suggested that a drained peatland should have a higher GWP than a restored peatland. However, of the six collars for which GWP could be calculated, two of the three collars from Site A and the one collar from Site B all had GWP values greater than those from collars C3 and C6 at the control site where

conditions are similar to when peat extraction was occurring. Both (Joosten et al., 2006; Bain et al., 2011) suggested that as time since peatland restoration increased, the GWP values should decrease. However, the annual CH_4 fluxes for Sites A and B are significantly higher than for Sites C and D. Of the few NEE calculations that were accepted, there was no clear pattern or differences between sites. In terms of CH_4 fluxes at Site D, based on Figures 2.1 and 2.2, a higher WTP would suggest more CH_4 release to the atmosphere through increased methanogenesis. Yet, the *Sphagnum* cover indicates that there may be more methanotrophic activity (Raghoebarsing et al., 2005). Therefore, it is unclear what effect a higher WTP would have on the CH_4 fluxes and GWP for Site D.

Due to the small number of collars from each site for which NEE and GWP could be calculated, and the lack of such data for Site D, statistical analyses on the effects of restoration on NEE and GWP could not be carried out. However, as Tables 4.3 and 4.5 show, the highest and lowest values for NEE and GWP were from collars both located on Site A. This within-site variability highlights that factors other than time since restoration management started are potentially important in determining CH_4 and CO_2 fluxes. Collar A2 had the lowest overall NEE and GWP, and also had the lowest CH_4 flux of all the collars at Site A (Figure 4.6a). In comparison to the other collars at Site A, collar A2 had the sparsest vegetation cover (*Eriophorum angustifolium*) and the lowest WTP. A sparser vascular plant cover would suggest that there may be less of a contribution to methanogenesis through root exudation and not as many transport pathways through aerenchyma for CH_4 to escape to the atmosphere. Also, a lower WTP may mean a greater abundance of methanotrophs due to a larger oxic zone, and so more CH_4 would be consumed and not escape to the atmosphere. However, a lower WTP would also suggest that R_{TOT} for collar A2 would be higher due to increased soil respiration in a larger oxic zone. Therefore, above-ground plant respiration may be the more significant contributor to R_{TOT} because collar A2 also has the lowest R_{TOT} of the three collars at Site A (see Table 4.4). Also, collars C2 and C3 have the lowest R_{TOT} values of the six collars in Table 4.4, which also indicates that ecosystem respiration may contribute more to R_{TOT}

than soil respiration. Figure 4.5b shows that at Site B, collar B3 had the lowest CH_4 flux, and like collar A2, B3 had the sparsest vegetation cover (dominated by *E. angustifolium*) and lowest WTP of the six collars at Site B.

As Table 4.5 and Figure 4.6 show, the annual CH_4 fluxes on a per-site basis were significantly different at (and between) Sites A and B compared to Sites C and D which were not significantly different from each other. The main differences between Sites A and B and Sites C and D, apart from time since restoration started, were vegetation cover and WTP. Sites A and B were dominated by both *E. angustifolium* and *Eriophorum vaginatum*, and the WTP at both sites was low when fieldwork started, but rose throughout the winter months and was above the peat surface for the majority of the summer months. Both Sites C and D had very low WTP for the entirety of the fieldwork period, with no vegetation cover at Site C, and a mixture of *Sphagnum cuspidatum*, emergent *Calluna vulgaris*, and one small tussock of *E. vaginatum* at Site D. The difference in vegetation cover between the sites was attributed to successional change. Although successional vegetation cover change is a function of time, the WTP is a combined result of environmental processes and land management. The WTP is a CH_4 flux driver for both Sites A and B. Two vegetation variables are in the model for Site B, and bare peat cover is a variable in Site A. Therefore, no firm conclusions can be made as to whether the CH_4 fluxes at Sites A and B are a result of changes with time or land management.

The emergent vegetation at Site D, coupled with the less-than-ideal state of the *S. cuspidatum* plants due to the low WTP have blurred the signal of CH_4 and CO_2 fluxes. None of the collars at Site D produced both a successful P_G and R_{TOT} model; for each collar only one of the two models were successful. As Figure 4.5 shows, with the exception of collar D1 at the start of the fieldwork period, collar D3 (the only collar with emergent *E. vaginatum*) produced fluxes that were increasingly larger than the other five collars as the growing season progressed. For the multiple regression analysis to find the drivers of CH_4 flux at Site D, the only

variable returned by a backwards multiple regression model was *E. vaginatum* cover. Given that *E. vaginatum* was only present in one collar, had the backwards model been accepted, the predicted fluxes upon application of this model would have been identical for the five other collars. Even in the accepted stepwise multiple regression model for Site D, *E. vaginatum* cover was one of only two variables included in the model.

Holman and Kechavarzi (2010) predicted that, with a seasonally varying WTP, the NEE for Thorne and Hatfield Moors would be between 1.5 and 5 kg m^{-2} yr^{-1}. Of the six collars for which NEE could be calculated (Table 4.4) the cumulative NEE was 5.7 kg m^{-2} yr^{-1}; 0.2 kg m^{-2} yr^{-1} higher than the prediction by Holman and Kechavarzi (2010). However, there were 18 collars for which NEE could not be calculated; were this data available, then the cumulative total could have included negative values (uptake), bringing the total down to the range of Holman and Kechavarzi (2010). Under the same conditions, Holman and Kechavarzi (2010) also predicted CH_4 loss from Thorne and Hatfield Moors to be between 30 and 2000 mg CO_2-e m^{-2} yr^{-1}. However, from the data presented in Table 4.5 of CO_2-e per site, the cumulative total is 4.6 kg CO_2-e m^{-2} yr^{-1}, and so the predictions of Holman and Kechavarzi (2010) are a large underestimation. Many of the CH_4 fluxes per site in Table 4.5 are larger than the annual fluxes found in the literature in Table 4.2.

4.5 Conclusions

This chapter aimed to address research questions 1 and 2:

1. **Do CH_4 and CO_2 emissions from peatlands change with time following restoration?**
2. **What are the main drivers of CH_4 and CO_2 emissions in restored peatlands?**

Despite the fact that NEE fluxes could not be estimated for every collar, where it could be, it showed that carbon was emitted to the atmosphere at all sites, and thus the GWP values were very large. The R_{TOT} values from the four collars at restored sites were larger than from the two collars at the control site. There were significant differences in CH_4 fluxes between the two older sites (A and B) and the younger restored site (D), and also between Sites A and B. However, there were also differences in WTP and vegetation cover between the two older and two younger sites; although, the differences in vegetation cover could be successional changes which are a function of time. Therefore, peatland restoration has not had the predicted effect that some studies (Bain *et al*. 2011; Joosten *et al*. 2006) have suggested. Although the dataset is small, gaseous fluxes of CO_2 and CH_4 to atmosphere have, overall, increased with time following restoration.

For research question 2, soil temperature was returned as the main driver of R_{TOT} at Sites A and B, with soil temperature and WTP as drivers of R_{TOT} at Site C. Solar radiation, and various combinations of WTP, soil temperature, air temperature and ETI were drivers of P_G at Sites A and B. However, due to the use of the approaches to CO_2 modelling by Tuittila et al. (1999) and Samaritani et al. (2011), these were the only variables inputted as training variables for the model construction. However, these drivers were only significant for six out of a total of 24 collars due to large variability within the datasets, particularly for P_G.

Time and financial constraints meant that measurements could not continue for more than 13 months; although, it is recognised that a comparison between at least two years of flux measurements would have been very useful to give an insight into any possible interannual variation in gaseous fluxes. A comparison between different years would have been especially useful with regards to Site D, where during the summer of 2011 the WTP fell to > 20 cm below the peat surface and never rose to a consistent position near the peat surface for the entire measurement period during 2012.

Chapter 5: Diurnal variation in methane and carbon dioxide fluxes

5.1 Introduction

5.1.1 General approaches to chamber flux measurements

Field measurements of methane (CH_4) and carbon dioxide (CO_2) fluxes using the static closed chamber method are often conducted during daylight hours *cf.* (Bowes and Hornibrook, 2006; Bubier, 1995; Pelletier et al., 2007; Strack et al., 2004). Static closed chamber tests are usually conducted over a short period of time: usually 20-30 minutes (Baird et al., 2009), but sometimes as long as 120 minutes (Bubier, 1995), because this method involves taking gas samples via syringe, to later be analysed via GC. Therefore, the test duration has to be long enough in order for a concentration change (if present) to be detected in the samples collected. However, portable gas analysers can significantly reduce test times (2 - 10 minutes) (Kim and Verma, 1992; Bubier et al., 2003) . The resulting fluxes from the field measurements are often calculated and reported in units of mg CH_4 m^{-2} day^{-1} and g CO_2 m^{-2} day^{-1} *cf.* (Waddington et al., 1998; Kim and Verma, 1992; Alm et al., 1999). Indeed, this approach has been taken in the work presented in Chapters 4 and 5 of this study. For CH_4 fluxes, this method of flux calculation relies on the assumption that the flux captured during the particular time period of measurement is steady, with no diurnal changes. If seasonal or annual fluxes are being calculated, then this assumption may be assumed to hold for up to two weeks between field measurements (Coulthard et al., 2009), because fluxes can be integrated over time using simple linear interpolation. A weighted-average approach could also be applied to CH_4 fluxes, with the assumption that the fluxes measured are constant for the time periods in between measurements, as has been done in Chapter 4 of this study. For CO_2, as fluxes are so heavily dependent on rates of photosynthesis and soil respiration, a modelling approach is often used in order to take the known diurnal variation into account (Kutzbach et

al., 2007; Samaritani et al., 2011; Tuittila et al., 1999; Wilson et al., 2007). In terms of CH_4 fluxes, how the system might be affected by diurnal changes in the controlling variables is not so clear; indeed what the controlling variables are is also unclear; therefore, a modelling approach is not usually taken (Ding et al., 2004; Laine et al., 2007). If CH_4 fluxes are different during the night compared to the day, then only taking measurements during daylight hours could potentially lead to an under- or overestimation of the fluxes in the system. Any under- or overestimation could then have a knock-on effect in terms of full gaseous carbon budgets for a system.

In the field, CH_4 flux measurements using static closed chambers often involve the chamber being covered by a shroud to prevent artificial warming inside the chamber during the measurement period, *cf.* (Van Den Pol-Van Dasselaar et al., 1999; Pelletier et al., 2007; Baird et al., 2009). Similarly, for CO_2 flux measurements, two measurement periods often occur consecutively, once without a shroud covering the chamber to allow light penetration and once with the shroud to block out the light and therefore simulate night-time conditions, *cf.* (Bubier et al., 1998; Heikkinen et al., 2002; Waddington and Roulet, 1996), which allows for a comparison of NEE and ecosystem respiration. Both of these measurement techniques for CH_4 and CO_2 flux measurements were adopted for the routine sampling detailed in previous chapters of this thesis (3, 4 and 5). However, the use of a shroud prevents photosynthesis during CH_4 flux measurements, which could have an effect on methanogenesis through substrate supply (examined in more detail in Section 6.1.3.1). For CO_2 flux measurements, whenever the chamber is shrouded all other environmental variables, particularly temperature, are still at daytime levels. Given that temperatures are often lower during the night-time, simply using a shroud does not thoroughly simulate night-time conditions. Therefore, there may be a bias in the results of CO_2 fluxes if they are only measured in the daytime, particularly with regards to ecosystem respiration, which then has a knock-on effect on calculations of NEE. The potential effects of

temperature on both CO_2 and CH_4 dynamics will be examined in further detail in Section 5.1.3.2.

5.1.2 Previous approaches to diurnal flux measurements

Some studies, as shown in Tables 5.1, have investigated the diurnal flux patterns of CH_4 in peatlands. Many of these studies were conducted during the growing season, when the microbial and plant functions that govern CH_4 dynamics in peatland are most active. From the studies shown in Table 6.1, there is no clear picture regarding diurnal flux patterns of CH_4 from northern peatlands. Fifteen studies show no diurnal pattern, 13 show daytime fluxes were greater than night-time fluxes and 3 show night-time fluxes were greater than daytime fluxes. However, these studies were conducted on a wide range of vegetation types. Of the studies shown within Table 5.1, there have rarely been more than one or two studies for any particular vegetation type. Mikkelä et al. (1995) found diurnal effects depended on the plant assemblages studied. Plant communities dominated by *Sphagnum* spp. displayed no diurnal patterns in CH_4 fluxes, whereas in plant communities dominated by vascular species, fluxes were significantly higher in the night than during the day (Mikkelä et al., 1995). In the vascular plant communities, the diurnal difference was suggested to be due to delayed delivery of substrate to methanogens for CH_4 production following maximum air temperatures or photosynthetically-active radiation (PAR) levels during the day (Mikkelä et al., 1995). Static closed chambers were used by Mikkelä et al. (1995); however, they were covered by shrouds preventing photosynthesis, which suggests that the authors refer to photosynthates fixed to the plants during the times the chambers were not in place. Therefore, there is a lack of information as to whether specific plant communities always display the diurnal flux patterns.

An examination of the literature for studies of diurnal CO_2 fluxes yields similar results to those shown in Table 5.1, in that many studies were conducted during the growing season summer months and over a wide range of vegetation types, *cf.*

(Hendriks et al., 2007; Yu et al., 2013; Lafleur et al., 2001). Many CO_2 studies have been conducted using eddy covariance (Lafleur et al., 2001; Yu et al., 2013; Hendriks et al., 2007; Neumann et al., 1994; Nieveen et al., 1998). Both Lafleur et al. (2001) and Nieveen et al. (1998) showed that PAR had the strongest control over CO_2 flux during the daytime, and night-time CO_2 fluxes were closely linked to soil temperature. Nieveen et al. (1998) showed an exponential relationship between night-time CO_2 flux and soil temperature at 2.5 cm depth (r^2 = 0.7), and a rectangular hyperbola relationship for net CO_2 exchange as a function of light (r^2 = 0.72). Panikov et al. (2007) measured CO_2 concentrations at 3 cm depth using a membrane probe array on peat cores exposed to diurnal light cycles, and also measured CO_2 fluxes in the surface headspace of these cores using a multi-gas analyser. The water-table position within the cores was approximately 5 cm below the moss "tips", which is assumed here to mean the capitula (Panikov et al., 2007). The vegetation at the surface of the cores consisted of *Sphagnum magellanicum, Sphagnum papillosum, Eriophorum angustifolium* and *Calluna vulgaris*, and the cores were taken from a mesotrophic bog in south-central Sweden (Panikov et al., 2007). The results showed that CO_2 uptake began instantaneously at the onset of light conditions, with soil CO_2 concentrations also increasing immediately (Panikov et al., 2007). The onset of dark conditions saw a switch in CO_2 fluxes to emissions and soil CO_2 concentrations began to linearly decrease (Panikov et al., 2007). These results of instantaneous switches suggest that there are no system lags involved in terms of carbon fixation by plants through photosynthesis and additions of carbon to the soil.

The majority of the studies shown in Table 5.1 use one of the three main methods for assessing CH_4 fluxes from peatlands: static closed chambers, automatic closed chambers or eddy covariance. For both CH_4 and CO_2 studies, fluxes measured using eddy covariance give an insight into diurnal fluxes on a field-scale, whereas closed chambers can give a more detailed insight with regards to the vegetation types contained within each chamber. However, where chambers contain multiple vegetation types, or the literature describes the vegetation on the study site in

general, but does not give specifics on individual collars, it can be unclear as to whether one specific vegetation type or a combination of types are contributing to a diurnal pattern, or a lack thereof. This problem can cause difficulty when comparing studies. Yu et al. (2013) showed how different measurement techniques can lead to different CH_4 flux results. Fluxes were measured using both a closed automated chamber system and eddy covariance in an area dominated by *Carex pamirensis, Carex alrofusca, Hippuris vulgaris, Triglochin palustre, Heleocharis* spp. and *Cremanthodium pleurocaule* (Yu et al., 2013). The closed chambers recorded maximum CH_4 fluxes during the night (22:00-00:00), whereas with eddy covariance, maximum CH_4 fluxes were recorded during the day (approximately 13:30) (Yu et al., 2013). The two different methods also showed difference in the timings of the lowest CH_4 fluxes: 10:00-12:00 for the closed chambers and 07:00 for eddy covariance (Yu et al., 2013). Both methods showed similar results and timings for CO_2 fluxes over a diurnal cycle (Yu et al., 2013). Therefore, the choice of measurement method and, if using collars, the choice of collar location (dominated by a single or multiple vegetation types) can both have impacts on diurnal flux studies.

Table 5.1: Results of studies examining diurnal CH_4 fluxes.

Patterns have only been classified when the literature stated that the daytime and night-time fluxes were significantly different ($p < 0.05$). .

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Bäckstrand et al. (2008)	Stordalen Mire, Sweden	June-August 2003-2006	Automatic closed chambers – measured total hydrocarbons which include CH_4	*Eriophorum angustifolium*	None	Daytime fluxes correlated negatively to NEE and positively to PAR, air temperature, air pressure and precipitation. Night-time fluxes correlated positively to NEE and air temperature and negatively to PAR.
				Sphagnum spp., *Carex rotundata, Eriophorum vaginatum, Rubus chamaemorus*	Day > night	Daytime fluxes positively correlated to soil temperature; night-time fluxes negatively correlated to NEE and positively correlated to soil temperature.
				Dry palsa site: *Andromeda polifolia, Empetrum hermaphroditum, Rubus chamaemorus, Eriophorum vaginatum, Polytrichum* spp., *Dicranum elongatum, Vaccinium uliginosum, Sphagnum fuscum, Betula nana*		Daytime fluxes positively correlated to air temperature, PAR and soil temperature, and negatively correlated to NEE

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Ding et al. (2004)	Sanjiang Mire, northeast China	August 2002	Open-ended chambers	*Deyeuxia angustifolia, Carex lasiocarpa*	Day > night	Lags related to sunrise/set. Significant relationship in *C. lasiocarpa* site between CH_4 fluxes and mean [CH_4] in porewater. No significant relationships with air or porewater temperatures.
Greenup et al. (2000)	Roudsea Moss, UK	July, August, October 1997	Through-flow chambers	*Eriophorum vaginatum, Sphagnum papillosum*	None	Diurnal pattern analysis based on mean fluxes from four chambers. No pattern either with *E. vaginatum* cover or just *Sphagnum* cover.
Hargreaves and Fowler (1998)	Blanket bog, Flow Country, UK	May-June 1994	Eddy covariance	Open water	Day > night	Pattern emerged when fluxes averaged over study period – no systematic variation when days looked at individually. Positive relationship between flux and soil temperature.
Kim et al. (1998a)	Ballards Marsh, Nebraska, USA	July-September 1993	Eddy covariance	*Phragmentes australis, Scirpus acutus*	Day > night	Fluxes strongly positively correlated to PAR, air temperature gradient within and above canopy and canopy conductance.

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Kim et al. (1998b)	Prairie marsh, Nebraska, USA	April-May – early growth	Eddy covariance	*Phragmites australis*	None	Emerging plants not above surface of ponded water. Molecular diffusion likely to be main transport pathway.
		May – prior to tillering			Day > night	Plants above water. Peak flux in late afternoon. No diurnal variation in sediment temperature. Diurnal variation in water temperature similar to flux variations.
		May-September – tillering to early senescence			Day > night	Correlation with changes in PAR and temperature difference between plant and ambient air. Rapid plant growth during this time.
		September-October - senescence			Day > night	Lower fluxes than during growth stages, but pattern still evident.

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Klinger et al. (1994)	Hudson Bay Lowland, Canada	July 1990	Static closed chambers	Not stated	None	No soil temperature pattern.
Laine et al. (2007)	Lowland blanket bog, Co. Kerry Ireland	All seasons	Static closed chambers	*Schoenus nigricans, Molinia caerulea, Erica tetralix, Rhynchospora alba*	None	Graphically, fluxes at night greater than the day, but statistical analyses not conducted. Fluxes related to changes in soil temperature at 20 cm depth.

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Long et al. (2010)	Fen, Alberta, Canada	Late May-June – early growing season	Eddy covariance	*Picea mariana, Larix larincina, Betula pumila, Sphagnum angustifolium, Sphagnum fuscum, Sphagnum* spp., *Drepanocladus aduncus, Aulocomnium palustre, Pleurozium schreberi, Triglochin maritima, Menyanthes trifoliata* and *Carex* spp.	None	None
		July – growing season peak			Day > night	Fluxes significantly positively correlated to solar radiation, net radiation, latent heat flux, ecosystem conductance and air temperature. No significant diurnal variation in soil temperature.
		August – post peak of growing season			None	None
		September – end of growing season / senescence			Day > night	None (no statistical tests reported)

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Mikkelä et al. (1995)	Mixed mire, Sweden	July 1991, August 1992	Dark static closed chambers – therefore not a true comparison of diurnal flux	Low ridges: *Sphagnum fuscum, Rubus chamaemorus, Oxycoccus quadripetalus,* Raised ridges: *Sphagnum fuscum* Minerotrophic lawn: *Sphagnum majus, Sphagnum balticum, Carex rostrata, Carex limosa*	Night > day	In August the pattern at the minerotrophic lawn was not significant.
		July 1991		Open pool with *S. majus* at bottom and edges	None	Release of CH_4 via ebullition during the day
		July 1991, August 1992		*Sphagnum*-dominated communities: *Sphagnum balticum, Eriophorum vaginatum*, mud-bottom communities with dead *S. majus*		One exception at a mud-bottom sampling location where day > night.
		September 1991		Low ridges (as above) Minerotrophic lawn (as above) Open pool (as above) *Sphagnum*-dominated communities (as above)		Fluxes significantly correlated with lagged soil temperature (2-8 hrs.) and lagged solar radiation (2-12 hrs.). Lack of pattern in ridges and minerotrophic lawn suggested to be due to lack of diurnal air temperature pattern on September sampling date.

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Shannon et al. (1996)	Buck Hollow Bog, Michigan, USA	1993 growing season	Static closed chambers	*Sphagnum* spp., *Scheuchzeria palustris, Vaccinium oxycoccos, Eriophorum virgincum, Chamaedaphne calyculata*	None	High flux late afternoon Low flux mid-morning. Correlated to lag in shallow peat temperature.
Thomas et al. (1996)	Ellergower Moss, UK	Unclear	Static closed chambers on cores in lab	*Sphagnum* spp., *Molinia caerulea, Eriophorum angustifolium, Carex echinata, Calluna vulgaris, Erica tetralix*	Day > night	Not real diurnal cycles, but fluxes significantly greater under artificial light than in darkness over 2-3 hrs.
Wang and Han (2005)	Inner Mongolia marshes	Summer: July, August	Dark static closed chambers	Sandy site: *Carex sabulosa, Carex appendiculata, Juncus wallichianus* Organic site: *Glyceria spiculosa, Scirpus planiculmis, Agrostis divaricatissima, Scirpus triqueter*	Day > night	Highest fluxes in late afternoon (sandy) or early evening (organic). Lowest fluxes just before sunrise.
		Winter: October, November			None	Double peak in CH_4 fluxes matched peaks in air temperature at sandy site.
Whalen and Reeburgh (1988)	Subarctic muskeg, Alaska	May, June, July 1987	Static closed chambers	*Eriophorum vaginatum*, *Sphagnum* spp., *Aulocomnium* spp., *Hylocomium* spp., *Tomenthypnum* spp., *Polytrichum* spp., *Carex aquatilis*	None	Diurnal variation in soil temperature; attributed to insolation.

Reference	Location	Time of year	Method	Vegetation	Pattern	Additional information
Yavitt et al. (1990)	Big Run Bog, West Virginia, USA	June, August 1988	Static closed chambers	*Sphagnum fallax, Sphagnum magellanicum, Eriophorum virginicum; Picea rubens, Sphagnum girgensohnii; Carex canescens*	Night > day	Not discussed
		October 1988			Day > night	
		June, August, October 1988		*Sphagnum fallax, Ilex verticillata, Pyrus arbutifolia, Viburnum cassinoides; Polytrichum commune, Rubus hispidus, Carex folliculata*	None	
Yu et al. (2013)	Luanhaizi wetland, China	July-September	Eddy covariance	*Carex pamirensis, Carex atrofusca, Hippuris vulgaris, Triglochin palustre, Heleocharis spp., Cremanthodium pleurocaule*	None	Highest fluxes at 13:30, lowest fluxes at 07:00. Daytime: positive correlation with solar radiation and net CO_2 fluxes. Night-time: positive correlation with soil temperature.
			Continuous automated chamber		Night > day	Positive correlation with soil temperatures, negative correlation with CO_2 sequestration, no relationship with solar radiation.

5.1.3 Diurnal changes in environmental variables

Many of the studies detailed above identified, through statistical analyses, environmental variables that caused diurnal pattern in CH_4 and CO_2 fluxes. This section examines two of the main controls on diurnal variability in fluxes of CH_4 and CO_2: PAR and temperature.

5.1.3.1 Photosynthetically-active radiation

Photosynthetically-active radiation is responsible for driving the rates of photosynthesis in plants. For CO_2 fluxes, a high value of PAR, and therefore a high rate of photosynthesis, should lead to high CO_2 uptake by the vegetation. In terms of CH_4 fluxes, some of the carbon fixed by plants via photosynthesis is transferred to the roots and then into the surrounding soil environment in the form of root exudates (chemicals emitted from roots into the soil) (Walker et al., 2003), where they then available as microbial substrates (Van Veen et al., 1989). For example, it has been noted that root exudates are an important substrate for methanogens (Bergman et al., 2000; Greenup et al., 2000; Megonigal et al., 1999; Saarnio et al., 1998). Increased methanogenesis due to input from photosynthates increases CH_4 production, and so possibly increases CH_4 fluxes to the atmosphere during daylight hours when photosynthesis is occurring, as opposed to during hours of darkness. However, this process depends largely on lag times from carbon fixation to root exudates to methanogenesis to transport up to atmospheric release. From a microcosm experiment using radiocarbon tracers, Megonigal et al. (1999) linked photosynthates in *Orontium aquaticum* (L.) to methanogenic activity in the surrounding soil system within 12 hours. This short lag time suggests that photosynthesis could influence CH_4 fluxes on a diurnal scale. From a study on a fen in Quebec, Canada, Whiting and Chanton (1992) found a positive correlation (r = 0.93) between CH_4 emissions and net CO_2 exchange from measurements taken between 28th July and 4th August 1990. The authors suggested that this link showed photosynthates enhancing rates of methanogenesis; however, any lags that may have been present between the processes were unquantified (Whiting

and Chanton, 1992). Using ^{14}C labelling in a pulse-chase experiment, performed by adding $^{14}CO_2$ to chambers housed over peat monoliths, Christensen et al. (2003) found that only 0.5 % of ^{14}C was detected as $^{14}CH_4$ over four months of monitoring the carbon flow in a monolith from an area dominated by *Eriophorum angustifolium*, *Sphagnum magellanicum* and *Sphagnum papillosum*. Christensen et al. (2003) suggested that this result indicates a long lag time within the system.

A complicating factor is that plants which supply substrate to methanogens often also supply O_2 to their rhizosphere and the O_2 may inhibit methanogenesis and enhance methanotrophy (Roura-Carol and Freeman, 1999). Ding et al. (2004) suggested that, in an area dominated by *Carex lasiocarpa*, photosynthesis could be contributing to increased rates of methanotrophy, rather than methanogenesis, through increased O_2 transport to the plant rhizomes and rhizosphere. Green and Baird (2011) indicated that when light is reduced, O_2 concentrations within plants are also reduced, because stomata close and thereby limit the supply of O_2 to the rhizosphere. A reduction in PAR also leads to a reduction in O_2 production in plants through photosynthesis (Green and Baird, 2011). If there is less O_2 reaching the rhizosphere during the night, there may be less methanotrophy and therefore a greater CH_4 flux to the atmosphere during the night. Overall, there does not appear to be a consensus within the literature as to whether CH_4 fluxes are influenced by PAR levels and photosynthesis on a diurnal scale.

5.1.3.2 Temperature

Both methanogenesis and methanotrophy are temperature-dependent (Dunfield et al., 1993; van Winden et al., 2012; Williams and Crawford, 1984). Williams and Crawford (1984) found that rates of methanogenesis declined with both temperature decreases (30-4 °C) and depth below the water table (10-210 cm). Valentine et al. (1994) linked the effect of temperature on methanogenesis to substrate quality, with temperature having an increased positive effect when better quality substrate was available. Frenzel and Karofeld (2000) measured

potential methanogenesis in peat samples from an Estonian raised bog and concluded that the Q_{10} values (the rate at which a reaction varies over 10 °C) ranged from 4.5 to 6.8 at a temperature range of 4-25 °C. From an experiment using peat slurries, Dunfield et al. (1993) found that methanogens have a stronger relationship with temperature change than methanotrophs. Methanogenesis rates (Q_{10} values of 5.3-16) reached a peak when temperatures were in the range of 25-30 °C, whereas methanotrophy rates (Q_{10} values of 1.4–2.1) were still very active at lower temperatures, with an optimum at 20-25 °C. van Winden et al. (2012) reported Q_{10} values for methanotrophy (10-20 °C) of 2.6. Higher soil temperatures should therefore lead to higher rates of methanogenesis and methanotrophy; although, if methanogenesis does have a stronger relationship with temperature, then CH_4 fluxes should increase with higher soil temperatures. Soil respiration, leading to the release of CO_2, is known to increase with increasing temperatures, *cf.* (Lloyd and Taylor, 1994; Raich and Schlesinger, 1992; Smith et al., 2003).

Air temperatures at night are generally lower than during the day, which would suggest that, if soil temperatures respond quickly to changes in air temperature then both CH_4 and CO_2 fluxes should decrease during the night. However, as CO_2 fluxes increase during the night, PAR appears to exert a stronger control over CO_2 fluxes. Although, if there is a lagged response from soil temperatures to changes in air temperatures then the increase of CO_2 fluxes at night could be accelerated due to increased soil respiration. If this is true, then measuring CO_2 fluxes from peatlands during the day using a shrouded chamber to simulate night-time conditions will not take account of this increased rate of respiration. Therefore, the recorded CO_2 fluxes may be an underestimation. This potential lag in soil temperature response could also mean that CH_4 fluxes may also increase during the night, meaning that fluxes measured during the daytime are also an underestimation.

5.1.4 Aim

Based on the literature reviewed above, there is no clear picture on how CH_4 fluxes are likely to vary diurnally with any of the main vegetation and land cover types found at the sites studied at Thorne and Hatfield Moors: *Eriophorum angustifolium*, *Eriophorum vaginatum*, *Sphagnum cuspidatum* and bare peat. *Sphagnum* spp. do release photosynthates (Fenner et al., 2004); however, unlike *Eriophorum* spp., *Sphagnum* mosses do not have roots that penetrate down into the anoxic layers where methanogenesis occurs (Thomas et al., 1996). Also, the *S. cuspidatum* at Hatfield Moor was in a degraded condition due to the low WTP at the site, so any further analysis into diurnal variation will focus on *Eriophorum* spp.. Fluxes from sites at Thorne Moors dominated by *Eriophorum* spp. have only been measured during daylight hours; therefore, if diurnal variation does exist, the annual and seasonal fluxes reported in previous chapters could be over- or underestimates, depending on the nature of any diurnal pattern found.

Therefore, the aim of this study was to address research questions 3 and 4:

3. **Do methane emissions vary diurnally, and if so, what are the main drivers of the diurnal variations?**
4. **Does the diurnal variation in CO_2 emissions result in positive or negative NEE?**

5.2 Methods

In order to address research questions 3 and 4, a study into CH_4 and CO_2 fluxes was conducted at Thorne Moors in July 2012 over one 24-hour period. Unfortunately time constraints inhibited any further measurement periods. Dates in summer were chosen as many of the studies detailed in Table 5.1 were also conducted in summer months, which should provide useful comparisons against the results of this study. The weather forecast was used to help define a 24-hour period when

there would be a diurnal change in temperature, because temperature is deemed to be important in terms of gaseous flux dynamics.

5.2.1 Site location and conditions

As previously outlined, areas dominated by *Eriophorum* spp. were most appropriate for this study; given their potential to affect gaseous fluxes on a diurnal scale due to root exudation. Site A, where restoration began in 1997, was chosen for this study because it was dominated by *Eriophorum angustifolium* and *Eriophorum vaginatum*. At the time the study occurred the site was under shallow surface inundation. More details on the site location and general site conditions can be found in Section 3.1.2 and Table 3.1. Four collars were analysed for this study: two dominated by *E. angustifolium* (A5 and A6) and two dominated by *E. vaginatum* (A1 and A4).

5.2.2 Flux measurements

Static closed chambers (as described in Sections 3.2.2.1 and 3.2.2.2) were used to measure CH_4 and CO_2 fluxes between 13:30 on 25th July and 12:00 on 26th July 2012. Three minor modifications were made to the chamber setup and measurement method, originally outlined in Sections 3.2.2.1 and 3.2.2.2, and the modified setup is shown in Figure 5.1. The first modification was to remove the shroud from each chamber to allow photosynthesis to occur during all measurements. The second modification was to hang a gel ice pack (140 x 130 mm, Value Products Ltd) inside each chamber during each test to prevent artificial warming inside the chamber due to the absence of the shroud (Bahn et al., 2009; Green and Baird, 2011) (except during the 06:00 tests where there were no ice packs available; however, the chamber temperature did not rise any more than it had done with the ice packs, most likely due to the early hour). The third modification was that both CO_2 and CH_4 concentrations (ppm) were measured from the same gas samples via GC to allow for more flux chamber tests to be

conducted overall. There were time constraints with running chamber tests for sample analysis via GC due to the lack of availability of a portable analyser that could measure both CH_4 and CO_2 concentrations instantaneously. Therefore, only unshrouded chamber tests were conducted, which meant that only NEE CO_2 fluxes could be measured. Static closed chamber tests ran for 23 minutes, every 90 minutes, with all four collars tested simultaneously. A total of 16 flux chamber tests were conducted on each collar. Each collar required an extension collar to account for tall vegetation, as described in Section 3.2.2.1. Gas samples were collected and analysed in the same way as described in Section 3.2.2.2, with one minor exception for the calculation of net CH_4 and CO_2 fluxes. Fluxes from each chamber test were calculated in the same way as described in Section 3.2.2.3, except that the mass flux density was multiplied by 5400 (the number of seconds in 90 minutes) instead of 86400 (the number of seconds in 24 hours) to give a flux of mg CH_4/CO_2 m^{-2} 90 $minutes^{-1}$. The fluxes were expressed per 90 minutes as that was the duration between the start of each chamber test. When all of these fluxes were added together, the result was the net flux in mg CH_4/CO_2 m^{-2} day^{-1} because 5400 multiplied by 16 is equal to 86400.

Figure 5.1: Chamber setup for diurnal sampling

5.2.3 Meteorological and environmental variable measurements

In order to determine the potential drivers of any diurnal variations that might be observed, the following environmental variables were measured alongside the gaseous sampling, based on evidence in the literature, as detailed in Chapter 2. Water-table position was measured from the dipwell adjacent to each collar during each test, as described in Section 3.2.3.1. Soil temperature at 10 cm depth (Squirrel Data Logger) and PAR levels at the vegetation surface (Skye Instruments) were measured adjacent to one collar during each test. These measurements were taken at a different collar in rotation for each test, because it was assumed that these variables would be uniform across the sampling area, given the minor variation in soil temperature that was observed during routine sampling when soil temperatures were measured consecutively in each collar on the site. Soil temperature and PAR were never recorded at the same collar at the same time. As described in Section 3.2.3.2, the AWS recorded hourly averages of variables including air temperature, barometric pressure, humidity, precipitation and wind speed and direction.

5.2.4 Statistical analyses

In order to test for a statistically-significant difference for both the CH_4 and CO_2 fluxes between the daytime and night-time, paired t-tests were used. For each gas separately, on a per-collar basis the fluxes were split into daytime and night-time according to the associated PAR reading (PAR > 0 = day, PAR = 0 = night), and then the mean flux for each collar at each time period was calculated, resulting in four mean flux values for the day and four mean flux values for the night. A paired t-test was then applied to these mean flux values. This analysis was carried out using Microsoft Excel 2010.

To test for a statistically-significant difference for both the CH_4 and CO_2 fluxes between collars dominated by *E. vaginatum* and collars dominated by *E.*

angustifolium, Mann-Whitney U tests were used. For each gas separately, the fluxes were separated according to the dominant vegetation type in the collar, then normality tests (Anderson-Darling, Minitab 16) were applied to the data. For CH_4 fluxes, those from collars dominated by E. angustifolium were not normally distributed ($p = 0.014$). For the CO_2 fluxes neither data set was normally distributed (*E. angustifolium*: $p = 0.026$, *E. vaginatum*: $p = 0.029$). Therefore, for both gases the non-parametric Mann-Whitney U test was applied, using Minitab 16.

Using the SPSS software package (IBM SPSS Statistics 19), multiple linear regression was applied to each collar, and for each gas, individually to determine the drivers of CH_4 fluxes and CO_2 fluxes. For both gases, the stepwise regression method yielded the best results in terms of the significanc of the model and the r^2 value. The independent variables included in each regression model were: PAR, soil temperature, air temperature, barometric pressure and the water-table position for the collar in question.

5.3 Results

5.3.1 Meteorological and environmental conditions

Table 5.2 shows the environmental variables that were measured on each sampling occasion: soil temperature, PAR levels and water table (WT) position. Sunset on 25/07/2012 was at 21:15, and sunrise on 26/07/2012 was at 05:11 (Time and Date website, 2013). From here on, daytime will refer to any time where PAR > 0, and night-time will refer to any time where PAR = 0. Figure 5.2 shows the hourly averages of air temperature and barometric pressure during the 24-hour sampling period. On 25th July air temperature reached a high of 20.8 °C from 14:00-16:00, and then declined to a low of 13.3 °C at 04:00 on 26th July. The temperature then rose to a high of 17.7 °C at 10:00 and again at 13:00. Prior to the start of the 24

hour period (13:00), the barometric pressure was steady at 1018.6 hPa from 14:00-18:00, and then it started to rise, reaching a high of 1021.8 hPa at 01:00. From this time it declined again to 1020.9 hPa at 07:00, then rose slightly to 1021.9 hPa at 08:00, then declined steadily for the remainder of the sampling time. There was no precipitation during the 24 hour sampling period.

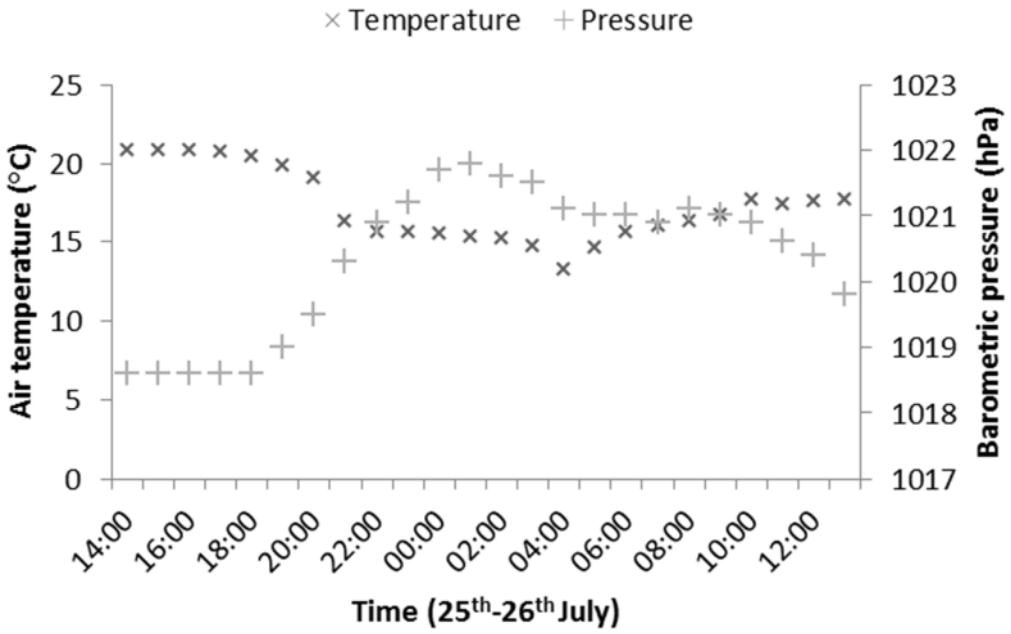

Figure 5.2: Hourly averages of air temperature and barometric pressure

5.3.1.1 Soil Temperature

Over the 24 hour period, soil temperature varied by 2.23°C, with the maximum and minimum temperatures occurring within 90 minutes of each other (at different collar locations) on 25th July. The lowest soil temperature, of 17.01 °C, was recorded at 15:00 and the highest, of 19.24 °C, was recorded at 16:30. During the night, soil temperature varied by just 1.4°C. The average daytime temperature was 17.92 °C and the average night-time temperature was 18.04 °C. As Figure 5.2 shows, the daytime air temperature was higher than the night-time temperature, which suggests that there is a lag in the response of soil temperature to changes in air temperature. Figure 5.3 shows a plot of the soil temperature measurements for each collar. These data show that the assumption of uniform soil temperature over

the entire sampling area at each sampling time was incorrect. The soil temperatures adjacent to each collar did not show the same temporal pattern. Soil temperatures adjacent to collars A1 and A4 declined as time progressed. However, at collar A5 there was a slight decline for the first three measurements recorded at 13:30, 19:30 and 01:30, but a slight increase at the last measurement recorded at 07:30. At collar A6 there was an increase between the first and second measurements recorded at 15:00 and 21:00, followed by a slight decline recorded at 03:00, and then a minor rise of 0.02 °C recorded at 09:00. The WT position at each collar is likely to have had an influence on soil temperature, which will be explained in the next section.

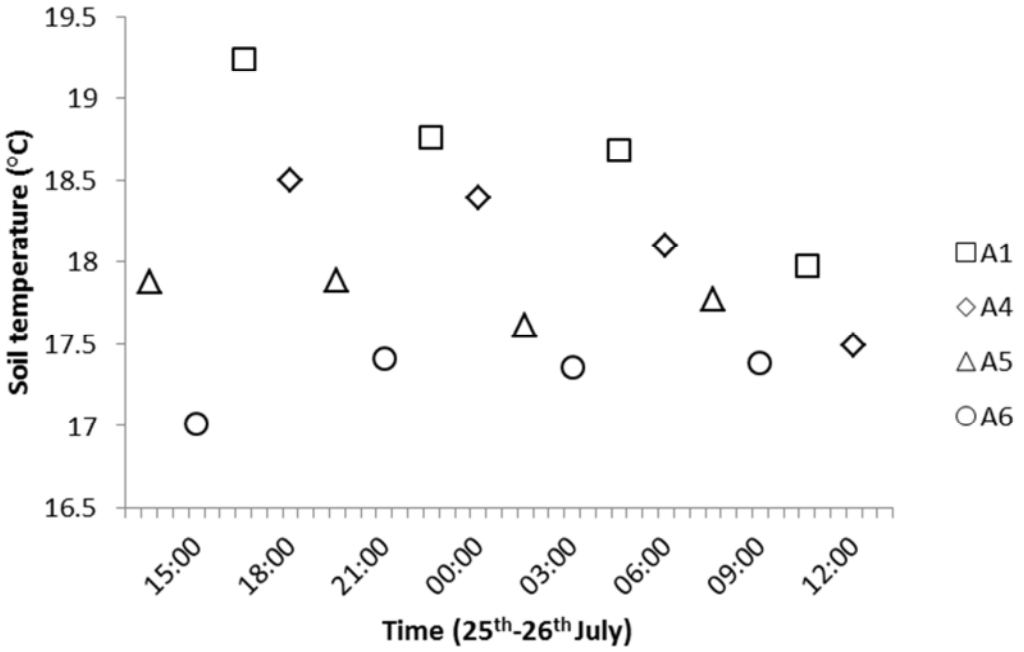

Figure 5.3: Soil temperature of each collar

5.3.1.2 Water table positions

Water table positions were fairly constant in each dipwell for the duration of the sampling period, with a maximum variation of 7 mm adjacent to collar A6. In all cases there was standing water above the peat surface, so positive WT values indicate depth of surface inundation. Average WT positions for the entire sampling

period for collars A1, A4, A5 and A6 respectively, were 30, 38, 96 and 93 mm. The shallower surface inundations were adjacent to the collars that experienced the greater variation in soil temperature (A1 and A4), as shown in Figure 6.2, whereas the collars where the range in soil temperature was smaller had deeper surface inundation. These differences in soil temperature suggest that the depth of surface inundation had an influence on how quickly the soil temperature responded to changes in air temperature.

Table 5.2: Environmental variables measured at each sampling time point

WTP = water table position. Positive values indicate depth of water above the peat surface. Shaded columns indicate night-time.

Time	**13:30**	**15:00**	**16:30**	**18:00**	**19:30**	**21:00**	**22:30**	**00:00**	**01:30**	**03:00**	**04:30**	**06:00**	**07:30**	**09:00**	**10:30**	**12:00**
Soil temp (°C)	17.88	17.01	19.24	18.5	17.89	17.41	18.76	18.39	17.61	17.36	18.68	18.1	17.77	17.38	17.98	17.49
PAR (μmol m^{-2} s^{-1})	620	500	280	280	40	0	0	0	0	0	0	90	250	270	450	390
WTP (mm) collar 1	31	31	29	30	29	30	30	30	30	32	28	30	28	30	28	30
WTP (mm) collar 2	40	40	40	37	39	35	35	36	39	39	37	38	38	38	38	39
WTP (mm) collar 3	96	95	97	94	98	96	95	95	98	98	97	93	96	95	95	96
WTP (mm) collar 4	88	94	95	93	92	95	95	94	94	95	94	92	93	93	91	90

5.3.2 Methane fluxes

Of the 64 chamber tests that were conducted, 62 CH_4 flux calculations were accepted and are presented here. Two fluxes had to be rejected, as shown in Table 5.3. A full description on how it was decided whether to accept or reject flux calculations can be found in Section 3.2.2.3. Table 5.3 also shows the net CH_4 flux over 24 hours for each collar.

Table 5.3: Discounted CH_4 flux times and net CH_4 flux over 24 hours per collar.
* indicates flux was rejected due to an r^2 value lower than 0.8, ‡ indicates flux was rejected for failing both criteria: the gradient of the regression line was insignificant and the r^2 value was lower than the threshold.

Collar	**Times of discounted fluxes**	**Net flux over 24 hrs. (mg CH_4 m^{-2} day^{-1})**	***n***
A1	None	62	16
A4	None	81.3	16
A5	03:00*, 07:30‡	48.8	14
A6	None	65.9	16

Figure 5.4 shows the CH_4 fluxes measured during the 24hr period, separated by vegetation type. When all four collars are considered together, the lowest flux of 35.6 mg CH_4 m^{-2} day^{-1} occurred at 01:30, with the highest flux of 94.9 mg CH_4 m^{-2} day^{-1} occurring just 90 minutes later at 03:00. The highest flux is more than double the lowest, which could have a big impact on flux calculations, ranging from the daily to annual scale. However, both of these fluxes occurred at night, so further analysis on a per-collar basis is needed. When the results for each collar are considered separately, the highest flux from each collar occurred during the night. With the exception of collar A5, the lowest flux for the remaining collars occurred during the day.

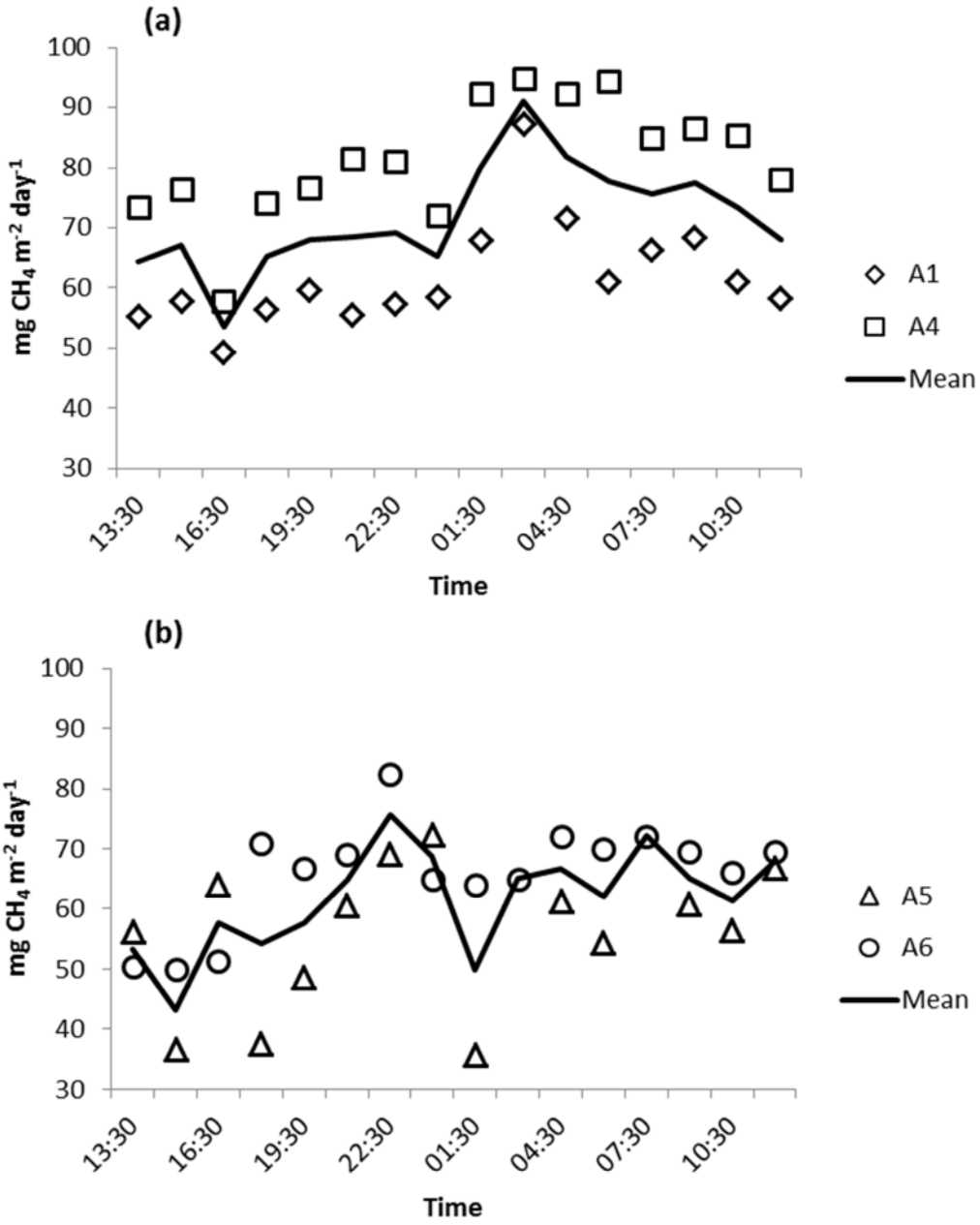

Figure 5.4: Methane fluxes over 24 hours for: (a) collars dominated by *E. vaginatum*, (b) collars dominated by *E. angustifolium*

Figure 5.4 also shows variation in the daytime fluxes, which could alone have an impact on up-scaling flux calculations. This variation is more pronounced on 25th July, and most so at collar A5, where over the six measurements taken prior to sunset, the resulting fluxes vary between 36.5 and 64 mg CH_4 m^{-2} day^{-1}. Table 5.4 shows a comparison between the maximum CH_4 fluxes recorded during routine

and diurnal sampling. This table shows that for collars A1, A4 and A6, the highest CH_4 fluxes recorded during the night-time of the diurnal measurement period were greater than the highest fluxes recorded for those same collars during the entire year of routine sampling, which was always conducted during the daytime. For collar A5 the highest flux recorded during routine sampling was only 2.5 mg CH_4 m^{-2} day^{-1} greater than the flux recorded during diurnal sampling. Overall, the difference in fluxes was much more pronounced for collars dominated by *E. vaginatum* (A1 and A4) than for those dominated by *E. angustifolium* (A5 and A6). Table 5.4 shows that diurnal sampling was conducted at the time of year where most of the highest CH_4 fluxes were recorded during routine sampling. In Table 5.4, the timing of the highest CH_4 flux in routine sampling for collar A1 is quite different than for the other three collars. If that date in October is excluded, then the highest CH_4 flux for collar A1 is on 16/08/2012 at 53.3 mg CH_4 m^{-2} day^{-1}, which is more in-line with the other three collars in terms of time of year. The differences between the maximum CH_4 fluxes during diurnal and routine sampling suggest that for areas dominated by *E. angustifolium*, the dark static closed chamber method employed during daytime sampling may be more accurate than for areas dominated by *E. vaginatum*, where this method may be underestimating CH_4 fluxes when up-scaled to a daily rate.

When the net CH_4 fluxes shown in Table 5.3 are compared to the CH_4 fluxes shown in Figure 5.4, a comparison can be made as to the times when the recorded CH_4 flux most closely matched the calculated net CH_4 flux. For collars A1 and A6 the fluxes recorded at 10:30 (61.1 and 66.1 mg CH_4 m^{-2} day^{-1} respectively) had the closest match to the net fluxes. For collar A4 the fluxes recorded at 21:00 and 22:30 (81.5 and 81.1 mg CH_4 m^{-2} day^{-1} respectively) had equally close matches to the net flux. For collar A5 the flux recorded at 19:30 (48.7 mg CH_4 m^{-2} day^{-1}) had the closest match to the net flux. These results show that collars dominated by the same plant species did not give fluxes that closely matched the calculated net fluxes at the same times, which suggests that the environmental variables affecting the fluxes may not be the same for the collars with the same plant species.

Table 5.4: Comparison of maximum CH_4 fluxes recorded during routine and diurnal sampling. Time refers to chamber test start times. Fluxes are in mg CH_4 m^{-2} day^{-1}.

Collar	Routine sampling			Diurnal sampling		Difference between fluxes
	Date	Time	Max CH_4 flux	Time	Max CH_4 flux	
A1	03/10/2011	16:52	55.3	03:00	87.3	32
A4	16/08/2012	12:27	75.9	03:00	94.9	19
A5	19/07/2012	18:13	74.7	00:00	72.2	-2.5
A6	19/07/2012	18:14	76.6	22:30	82.3	5.7

5.3.2.1 *Eriophorum vaginatum* collars

The highest and lowest fluxes from collars A1 and A4 occur at the same times (03:00 and 16:30 respectively), which suggests a diurnal pattern of night-time fluxes greater than daytime fluxes for areas dominated by *E. vaginatum*. The fluxes from collar A4 are consistently larger than those from collar A1. The differences between the highest and lowest fluxes at collars A1 and A4 are very similar at 38 and 37.1 mg CH_4 m^{-2} day^{-1} respectively. This diurnal variation suggests that fluxes from collars containing *E. vaginatum* could be underestimated if fluxes are only measured during the daytime. This point is also supported by the differences shown between the highest daytime fluxes from routine sampling and the highest fluxes recorded during diurnal measurements in Table 5.4.

5.3.2.2 *Eriophorum angustifolium* collars

The highest fluxes from collars A5 and A6 are 90 minutes apart at 22:30 and 00:00. The lowest fluxes for each of these collars are 10.5 hours apart at 15:00 and 01:30. The highest and lowest fluxes for collar A5 occur just one sampling period (90

minutes) apart, with a difference between the two fluxes of 36.6 mg CH_4 m^{-2} day^{-1}. The difference between the highest and lowest fluxes at collar A6 was 32.4 mg CH_4 m^{-2} day^{-1}. These results suggest that there is no obvious diurnal flux pattern for areas dominated by *E. angustifolium*. There were statistically-significant differences (p = 0.0086) between CH_4 fluxes recorded at the E. vaginatum collars and the E. angustifolium collars. This result suggests that the environmental variables controlling the CH_4 fluxes are different between the two vegetation types

5.3.2.3 Mean CH_4 fluxes

When all the fluxes from all four collars are split into daytime and night-time and averaged, the mean daytime flux is 64.1 mg CH_4 m^{-2} day^{-1} and the mean night-time flux is 70.8 mg CH_4 m^{-2} day^{-1}. Paired t-tests showed that there were significant differences between CH_4 fluxes during the day and the night (p = 0.00013). Therefore, overall night-time fluxes were greater than daytime fluxes, which suggests that only taking CH_4 flux measurements during the day leads to an underestimation in the quantity of CH_4 released from the system.

5.3.3 Fluxes of net ecosystem carbon dioxide exchange

Of the 64 chamber tests that were conducted, 49 NEE flux calculations were accepted and are presented here. The collar numbers and times of the 15 rejected fluxes are shown in Table 5.5. A full explanation of the criteria that fluxes had to meet to be accepted can be found in Section 3.2.2.3.

There is a clear diurnal pattern within the NEE fluxes, as shown in Figure 5.5, which also shows the corresponding PAR levels at each sampling time point. As expected, all negative NEE (CO_2 uptake) occurs during daylight hours, with the greatest uptake rate of 10316 mg CO_2 m^{-2} day^{-1} at 12:00 from collar A6. The highest rates of positive (CO_2 release) occurred during the night-time, with the highest flux of

43370 mg CO_2 m^{-2} day^{-1} at 03:00 from collar A1. A paired t-test showed that the NEE fluxes between daytime and night-time were significantly different (p = 0.00188), as was expected. The fluxes from each collar are very similar at each sampling time, although the range increases between 01:30 and 04:30. A Mann-Whitney U test indicated that there were no significant differences (p = 0.453) between NEE fluxes from collars dominated by *E. angustifolium* and collars dominated by *E. vaginatum*, which suggests that the two species behave similarly to the drivers of NEE fluxes.

Table 5.5: Discounted NEE flux times and total NEE flux over 24 hours per collar. Positive values indicate net release to the atmosphere. * indicates flux was rejected due to an r^2 value lower than 0.8, ‡ indicates flux was rejected for failing both criteria.

Collar	Times of discounted fluxes	Total NEE flux over 24 hours (mg CO_2 m^{-2} day^{-1})	*n*
A1	15:00‡, 07:30‡, 09:00‡, 10:30‡	15805	12
A4	13:30*, 16:30‡, 18:00‡, 07:30‡	10252	12
A5	13:30‡, 15:00‡, 07:30‡, 12:00‡	11863	12
A6	18:00‡, 19:30‡, 07:30‡	10053	13

Overall, there is a net loss of CO_2 from the system, despite the uptake in the peak daylight hours. Table 5.6 shows, for each of the four collars, the NEE fluxes recorded during the night-time are much larger than the highest-recorded NEE fluxes during routine sampling. These larger fluxes recorded during the night time show that efforts in the daytime to simulate night-time conditions purely by covering the flux chamber with a shroud are insufficient in replicating all night-time conditions. It should be noted for Table 6.6 that the methods by which CO_2 fluxes were measured is different, because routine sampling involved using an IRGA, as detailed in Section 3.2.2.2.

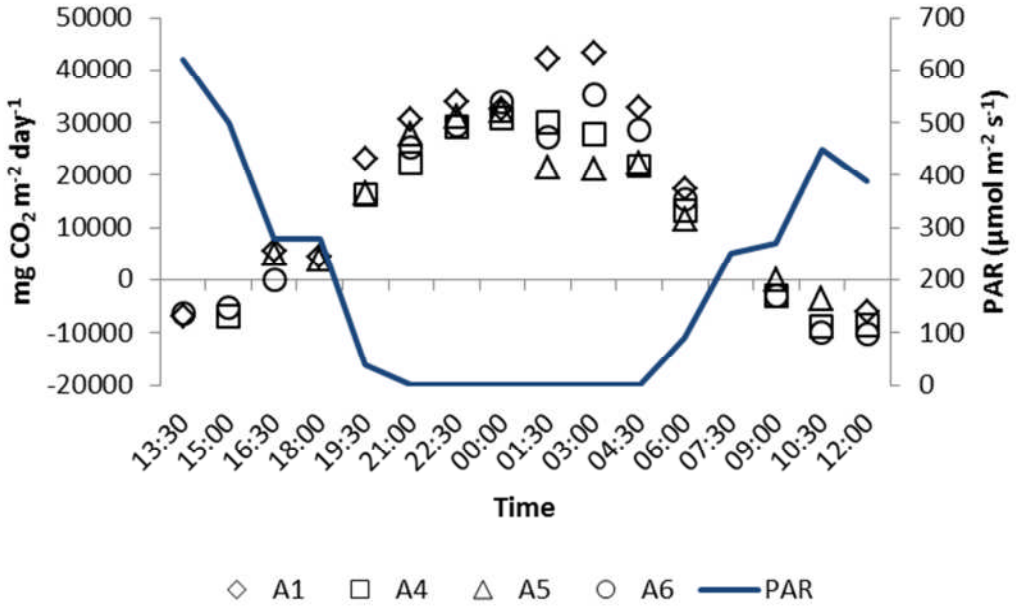

Figure 5.5: NEE fluxes from each collar and PAR levels over 24 hours

Table 5.6: Comparison of maximum CO_2 fluxes between routine and diurnal sampling. Time refers to chamber test start times. Fluxes in mg CO_2 m^{-2} day^{-1}.

Collar	Routine sampling			Diurnal sampling		Difference between fluxes
	Date	Time	Max CO_2 flux	Time	Max CO_2 flux	
A1	03/10/2011	15:30	29978	03:00	43370	13392
A4	19/07/2012	16:03	20940	00:00	30866	9926
A5	19/07/2012	15:48	21379	00:00	32214	10835
A6	20/06/2012	13:36	21383	03:00	35408	14025

5.3.4 Identifying flux drivers

Multiple linear regression was applied to each collar individually to determine the drivers of CH_4 flux. In collars A1 and A6, CH_4 flux was found to be driven only by air temperature (as shown in Figure 5.6) and in collar A4, CH_4 flux was driven by both air and soil temperatures (p = <0.001). However, for collar A5, no drivers could be found. Interestingly, although there was a statistically-significant difference between the CH_4 fluxes from collars dominated by *E. angustifolium* and *E. vaginatum*, Figure 5.6 shows that collars A1 and A6 have a very similar relationship with response to changes in air temperature. In terms of the results for collars A1 and A6, a decline in air temperature leading to a rise in CH_4 emissions is not what was expected, due to the positive relationship portrayed in the literature between air temperature and methanogenesis. There is also a positive relationship portrayed between air temperature and methanotrophy; however, this relationship is shown to be weaker than for methanogenesis. Therefore, these results point to a potential lag in the response of microbial activity to changes in air temperature. To investigate this possibility, air temperature was lagged at 90-minute intervals over the previous 24 hours and, using stepwise multiple linear regression, these lags were individually tested against the CH_4 fluxes from collars A1 and A6 along with the other environmental variables. The lag at 13.5 hours was found to be the best driver, and no other variables were entered into the regression model, shown in Figure 5.7. No other variables were entered into the regression model, as they were not deemed, by the statistical software, to add any improvement to the model further to that supplied by the variable of lagged air temperature at 13.5 hours. As Figure 5.2 shows, air temperature was higher in the day and lower in the night, as would be expected for most days. The potential lagged response shown in Figure 5.7 indicates that this cyclical air temperature pattern is switched, or shifted by almost one 12 hour wave cycle.

Multiple linear regression was also applied to each collar to determine the main drivers of CO_2 flux. The stepwise method resulted in PAR being the only driver of

NEE flux in each of the four collars, as shown in Figure 5.8. From the results in Figure 5.8, it would appear that once PAR levels exceeded approximately 400 µmol m^{-2} s^{-1}, NEE flux did not exceed (in the negative sense) approximately -10000 mg CO_2 m^{-2} day^{-1} in any of the four collars. This lack of response to increasing PAR levels suggests that at these higher PAR levels other environmental controls became the limiting factors for regulating NEE fluxes. Also shown in the data in Figure 5.8 is the wide range of fluxes that occur during the night when PAR is zero. At each collar during the night fluxes range over approximately 10000 mg CO_2 m^{-2} day^{-1}. This range of fluxes suggests that at night-time there are other environmental controls on NEE flux; however, as PAR exerts the strongest overall control, the stepwise regression model does not identify these other controls. When CO_2 fluxes from the night were analysed per collar using stepwise regression, a significant relationship (p = 0.001, r^2 = 0.96) was found for CO_2 fluxes from collar A5 and water-table position. No significant relationships were found for any other collars.

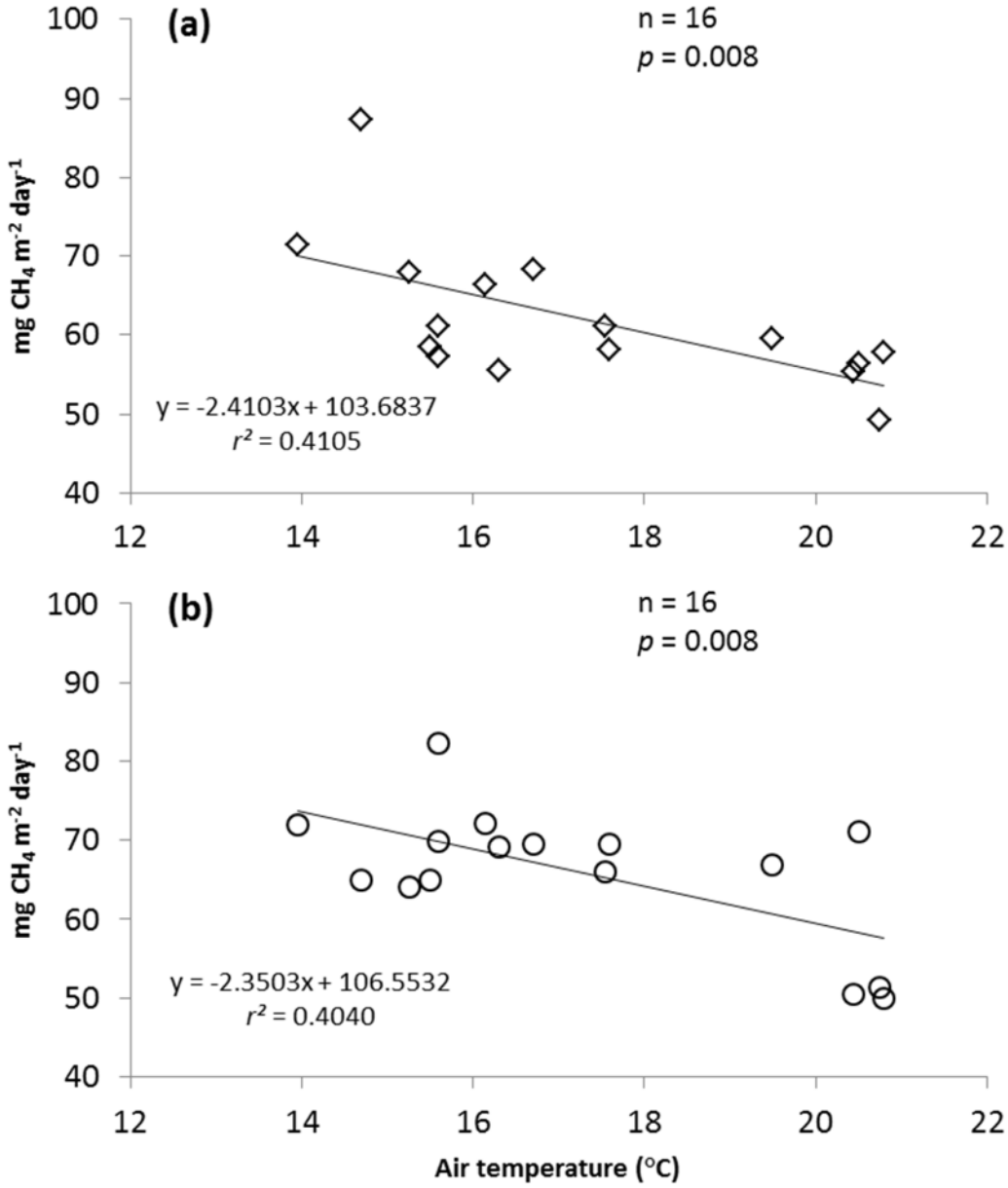

Figure 5.6: The linear regression between air temperature and CH_4 flux for: (a) collar A1, dominated by *E. vaginatum*, (b) collar A6, dominated by *E. angustifolium*

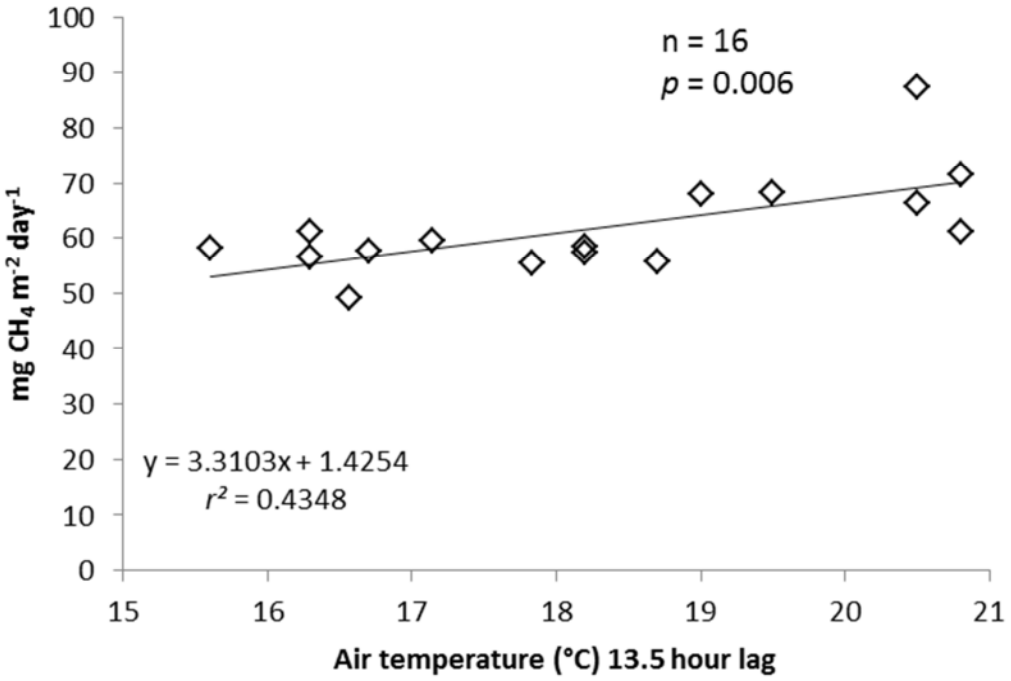

Figure 5.7: The linear regression between air temperature lagged by 13.5 hours and CH_4 flux at collar A1.

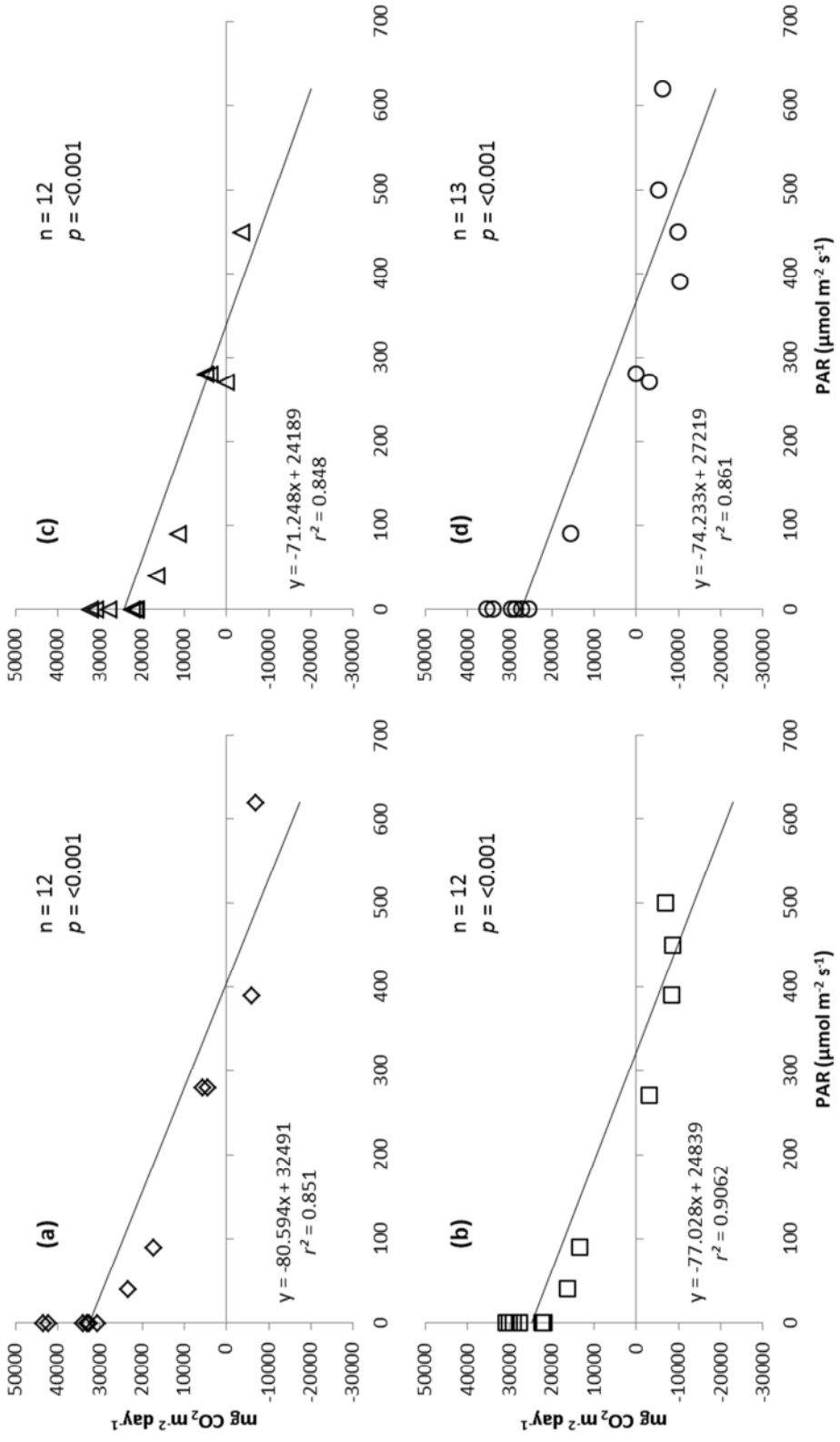

Figure 5.8: The linear regression between PAR and CO_2 flux for (a) collar A1; (b) collar A4; (c) collar A5; (d) collar A6

5.4 Discussion

5.4.1 Flux patterns

Methane fluxes were significantly different between day and night, with mean night-time fluxes greater than mean daytime flues, which accords with only 3 of the 31 sub-studies outlined in Table 5.1 (Mikkelä et al., 1995; Yavitt et al., 1990; Yu et al., 2013). Each of these studies occurred during summer months between June and September. Yavitt et al. (1990) conducted another diurnal study in October in the same location as in both June and August. The October study found a reverse in the diurnal flux pattern, with daytime fluxes significantly greater than night-time fluxes, which suggests that seasonality has an influence on diurnal flux patterns (Yavitt et al., 1990). The diurnal element appears to have been a small part of a much larger study by Yavitt et al. (1990), and so the drivers behind the observed diurnal flux patterns are not examined. In terms of the methods employed to measure fluxes, Mikkelä et al. (1995) and Yavitt et al. (1990) used static closed chambers; although Mikkelä et al. (1995) used dark closed chambers, and so the daytime fluxes were measured with the absence of light, which may have influenced the results. Yu et al. (2013) used continuous automated chambers and found that when fluxes from the same area measured by eddy covariance were analysed, no diurnal pattern was found. This difference in results highlights the variation that can occur when the spatial scale of the measurement method changes (Yu et al., 2013). Mikkelä et al. (1995) reported maximum CH_4 fluxes much lower than those recorded in this study. The maximum CH_4 flux recorded in July was < 36 mg CH_4 m^{-2} day^{-1} and in August was < 24 mg CH_4 m^{-2} day^{-1} (Mikkelä et al., 1995). Yu et al. (2013) recorded mean fluxes between approximately 149 and 180 mg CH_4 m^{-2} day^{-1}, which are larger than the fluxes recorded for this study. Yavitt et al. (1990) recorded fluxes between 0 and approximately 350 mg CH_4 m^{-2} day^{-1}, which cover a much larger range and reach a higher maximum than this study. Some of these differences could be due to the different vegetation types in each study. There were several *Sphagnum* species in the areas studied by Mikkelä et al. (1995), and areas dominated by bryophytes such as *Sphagnum* often have lower

CH_4 fluxes than areas dominated by vascular plants, such as *Eriophorum* (McNamara et al., 2008; Bowes and Hornibrook, 2006; van Winden et al., 2012).

In terms of the studies in Table 5.1 that were conducted on similar plant assemblages to this study, Greenup et al. (2000) studied an area on a lowland raised bog dominated by *E. vaginatum* and *S. papillosum*, and found no diurnal pattern in CH_4 flux in July, August or October. Greenup et al. (2000) only present data from their October measurements and their fluxes for areas dominated by *E. vaginatum* are comparable to those measured at collars A1 and A4. However, the study by Whalen and Reeburgh (1988) included one collar placed over an *Eriophorum vaginatum* tussock. The highest flux in the Whalen and Reeburgh (1988) study was recorded during the night and the lowest flux during the late afternoon, but overall there was no statistically significant flux pattern. However, the study was conducted in a tundra environment, and so the fluxes were lower than in the present study at 10 – 16 mg CH_4 m^{-2} day^{-1}. Bäckstrand et al. (2008) were investigating fluxes of total hydrocarbons, rather than CH_4 alone; however, two of the collars measured contained just *E. angustifolium*. Yet there was no significant diurnal pattern was reported (Bäckstrand et al., 2008) None of the other studies in Table 5.1 were conducted in areas dominated by *E. angustifolium* or *E. vaginatum*.

As expected, the diurnal pattern observed in the NEE fluxes from this study agrees with other studies looking at diurnal CO_2 fluxes: during the night-time, fluxes were positive and during the daytime fluxes were either negative, or if positive were much smaller (closer to zero) than during the night (Hendriks et al., 2007; Lafleur et al., 2001; Neumann et al., 1994; Nieveen et al., 1998; Yu et al., 2013). Overall the total NEE fluxes for the 24 hour period of study were positive for all four collars, despite the study taking place on a warm summer day when carbon fixation to plants via photosynthesis should be at a peak. Yu et al. (2013) found that CO_2 fluxes ranged from 12000 to -30000 mg CO_2 m^{-2} day^{-1}. The study by Hendriks et al.

(2007) was conducted over three years 2004-2006 showed that in each year the NEE varied within July between positive (release) and negative (uptake); although the majority of the NEE values for July in each of the three years were negative.

5.4.2 Flux drivers

The statistical analyses showed that temperature was the main driver of CH_4 fluxes in three of the four collars studied; specifically air temperature in collars A1 and A6, and both air and soil temperatures in collar A4. However, air temperatures are driven indirectly by solar radiation warming the Earth surface. PAR makes up part of the spectrum of solar radiation (400-700 nanometres (nm)), yet PAR was not selected by the regression analysis as a driver of CH_4 flux. The band of solar radiation that warms the Earth, and will therefore influence air temperatures is infrared radiation, which occupies 700 nm to 1 mm of the solar radiation spectrum; hence the reason that PAR was not selected by the regression analysis, because it is not responsible for warming the Earth surface.

Despite the collars being dominated by different species of *Eriophorum*, collars A1 and A6 displayed very similar relationships with air temperature, as shown in Figure 5.6. However, although collar A6 does show a maximum CH_4 flux during the night and a minimum CH_4 flux during the day, the timings do not correspond with those found at collar A1. These timing differences suggest that there are other factors, not just temperature, affecting the differences in flux patterns. The two main differences between these collars are vegetation species and depth of surface inundation. However, in the regression analyses performed on the data, depth of surface inundation was not returned as a controlling variable. This lack of return in the regression analysis of depth of surface inundation would suggest that it is in fact vegetation type controlling the difference in flux patterns. However, this does not explain why collar A5 did not show similar results to collar A6.

Figure 5.2 shows the air temperatures recorded over the 24-hour period of this study. There is a diurnal pattern to the air temperature in that it declines during the evening, reaching a low at 04:00 and then increase again during the early morning. Figure 5.6 shows a negative relationship between air temperature and CH_4 flux. Many of the studies shown in Table 5.1 found relationships between CH_4 fluxes and temperature; sometimes air (Wang and Han, 2005; Long et al., 2010; Bäckstrand et al., 2008) or water (Kim et al., 1998a; Wang and Han, 2005), but mostly soil temperature (Hargreaves and Fowler, 1998; Bäckstrand et al., 2008; Laine et al., 2007; Yu et al., 2013; Wang and Han, 2005). The majority of these relationships were positive, with the exception of the relationship between water temperatures and CH_4 flux at the sandy waterlogged site studied by Wang and Han (2005). The differences between those studies which find soil temperature to be the main driver of CH_4 flux, and this study where air temperature has been classified as the main driver could be related to the surface inundation reported in this study. The surface inundation may have an insulating effect on the response of soil temperature to changes in air temperature. Indeed, there are no significant correlations between air and soil temperatures ($p > 0.8$). If soil temperature had been measured at each collar at each test time, a clearer picture of the relationship between air and soil temperatures may have become apparent.

Ding et al. (2004) studied diurnal variation in a marshland dominated by the sedge species *C. lasiocarpa*. A lag of approximately four hours was found between sunrise and maximum CH_4 emissions, and between sunset and minimum CH_4 emissions was a lag of approximately five hours. Shannon et al. (1996) found a lag between maximum and minimum peat temperatures and CH_4 fluxes, and both lags were between one and five hours. Neither of these studies reported a significant differences between daytime and night-time fluxes (Ding et al., 2004; Shannon et al., 1996). Mikkelä et al. (1995) initially found a negative relationship between CH_4 flux and soil temperature; however, a lag in the temperature results of between 2 and 12 hours resulted in the relationship becoming positive. Figure 5.7 shows the only potential evidence of a system lag related to air temperature, where for collar

A1 a 13.5 hour lag was found to result in a significantly positive relationship between air temperature and CH_4 flux. A similar relationship was not found for collar A6, which suggests different responses from the two vegetation species. The current air temperature was returned by the regression analysis to be the only significant predictor of CH_4 flux, which indicates that there was not a system lag. This significant negative relationship between air temperature and CH_4 flux was reversed by lagging air temperatures over 13.5 hours, and so may not be evidence of a system lag. A pulse-chase isotope-labelling experiment would be a better way to identify if there was a system lag.

Some studies have attributed different fluxes between day and night to a change in the main transport pathway that takes CH_4 from the peat to the atmosphere. From a lab-based study examining gaseous concentrations at depth within and fluxes from the surface of peat monoliths, Thomas et al. (1996) concluded that a control on diurnal patterns may be related to stomatal opening and closure, through both gaseous release to the atmosphere and transport of O_2 down to the rhizosphere. However, Greenup et al. (2000) suggested that for *E. vaginatum*, stomatal opening and closure did not have an effect on diurnal CH_4 flux patterns; no evidence was found of diurnal patterns in any of the data. The data for this study in Figure 5.4a do show a diurnal pattern, but one that contradicts CH_4 transport to atmosphere being regulated by stomatal opening and closing, which agrees with the findings of Greenup et al. (2000). Stomatal closure limits the supply of O_2 to the rhizosphere of plants could inhibit methanotrophy in the rhizosphere; a process that has been studied extensively in rice paddies *cf.* (Epp and Chanton, 1993; Frenzel et al., 1992; Holzapfel-Pschorn et al., 1986; Van der Gon and Neue, 1996). If methanotrophy was inhibited during the night due to a lack of O_2, then CH_4 emissions would be expected to be greater at night; a theory which fits with the results of this study. However, Frenzel and Rudolph (1998) conducted a study into methanotrophy within *E. angustifolium* and *E. vaginatum* and concluded that methanotrophy made no significant contribution to the regulation of CH_4 emissions associated with these

plant species. This finding indicates that methanotrophic shutdown due to a lack of O_2 is not a process that has affected the results of this study.

Once PAR levels reached levels higher than approximately 400 µmol m^{-2} s^{-1}, NEE flux did not exceed (in the negative sense) approximately -10000 mg CO_2 m^{-2} day^{-1} in any of the four collars. Therefore, at these higher PAR levels other environmental controls may have become the limiting factors for regulating NEE fluxes. Alternatively, PAR levels of 400 µmol m^{-2} s^{-1} may have been the limit to the efficiency of the *Eriophorum* plants. Defoliart et al. (1988) indicated that, in *E. vaginatum* plants, younger leaves had higher photosynthetic capabilities than older leaves; however, it is unknown how old the leaves of the plants in collars were at the time of study. Gebauer et al. (1998) found that both *E. angustifolium* and *E. vaginatum* had comparable photosynthetic responses to light from a study based in an arctic tundra environment; a relationship that appears to be evident in the data presented here in that negative NEE (CO_2 uptake) in both species did not increase when PAR levels increased over 400 µmol m^{-2} s^{-1}.

The relationship between NEE and PAR is perhaps further evidenced by the times of the failed flux tests, as shown in Table 6.5. As Figure 5.5 shows, there are two step-changes in PAR: at 16:30 – 18:00 and 07:30 – 09:00. Of the 15 failed flux tests, eight occur during these step-change time periods. Prior to the first step-change, the majority of the fluxes are negative, followed by positive fluxes until the next step change, which starts at 07:30 where none of the fluxes calculated from tests at this time could be accepted. After the second step-change, the fluxes revert to negative values. This highlights the onset of photosynthetically-driven CO_2 uptake overtaking the effects of respiration-driven CO_2 release.

5.5 Conclusion

This study found that CH_4 fluxes were significantly greater during the night-time, which has implications for the preference of many researchers to only conduct CH_4 flux measurements during the daytime, because CH_4 fluxes are likely to be underestimations. In terms of NEE fluxes, there was a net loss of CO_2 to the atmosphere from each collar despite the study period occurring on a warm summer day. Also, the highest CO_2 fluxes recorded during the night-time were larger than the CO_2 fluxes measured using a dark static chamber in the daytime, as detailed in previous chapters of this thesis. Therefore, methods employed to simulate night-time conditions during the daytime do not achieve the desired effect, leading to underestimations of ecosystem respiration in dark conditions.

Air temperature was shown to be the main driver of CH_4 flux for two of the four collars measured, although the negative relationship between these two variables was unexpected, but did not indicate a system lag. Further work using labelled isotopes would allow for a more accurate identification of a system lag, if it did exist. Levels of PAR were shown to be the main drivers of CO_2 flux, but only to levels of approximately 400 µmol m^{-2} s^{-1}.

It is recognised that the data collected for this study are only from one diurnal cycle and only from two varieties of *Eriophorum*. Therefore, the results presented in this chapter are more observational than scientifically robust. However, these results provide an interesting insight into the potential issues with only conducting chamber flux tests during daylight hours. Measuring one 24-hour cycle on two collars of two different vegetation species does not allow for wider conclusions to be drawn as to whether the patterns in the fluxes measured were usual or irregular. Another limitation was that only NEE CO_2 could be measured due to the lack of availability of an instrument such as the portable GHG analyser from Los Gatos Research. The use of such an instrument would have allowed for light (NEE)

and dark (R_{TOT}) flux chamber tests to be conducted during daylight hours, providing a comparison of the potential differences in these results during the daylight hours. Also, different meteorological conditions are likely to result in differences in fluxes. More collar replicates would also have provided more flux data, from which a clearer pattern may have emerged. Very few studies have investigated diurnal fluxes outside of the summer season. Therefore, a wider study where diurnal studies were repeated over multiple days and seasons, and also captured a range of meteorological conditions would give a much greater insight into the true diurnal cycles of gaseous fluxes in areas dominated by *E. angustifolium* and *E. vaginatum*. Areas dominated by *Sphagnum* or bare peat could have diurnal variations in CH_4 and CO_2 fluxes due to changes in soil temperature. Therefore, further study comparing fluxes from these areas against the *Eriophorum*-dominated areas focussed on in this study may give an insight as to whether this assumption is true.

Chapter 6: Methanotrophy and *Sphagnum* mosses: a mutually-beneficial relationship affected by drought?

6.1 Introduction

6.1.1 *Sphagnum* mosses

Sphagna are bryophytes that have adaptations which enable survival in peatland environments. Each individual plant has a capiltulum at the top of a stem, with branches growing on the stem and leaves growing from both the stem and branches (Rydin and Clymo, 1989). The cells in the leaves consist of chlorophyllose cells, where all of the photosynthetic activity occurs, and larger hyaline cells, which are dead and often filled with water (Rydin and Jeglum, 2013). Solutes and bacteria can move in and out of the hyaline cells (Raghoebarsing et al., 2005; Rydin and Clymo, 1989). Lewis (1988) and Thompson and Waddington (2008) suggested that hyaline cells exist to provide structure and water transport within *Sphagnum* plants. *Sphagnum* mosses can grow in the acidic conditions (pH < 4) often found in peatlands and can endure very low concentrations of solutes (Clymo, 1970). Different species are found in different conditions; for example, *Sphagnum cuspidatum* prefers wet environments, with a high (near-surface) water-table position, whereas *Sphagnum rubellem* is found in drier environments (Rydin and Jeglum, 2013). However, Andrus (1986) reported that, in general, *Sphagnum* mosses are xerophytic hydrophytes, thriving in wet conditions, but have adaptations to deal with periods of drought. *Sphagnum* leaves are only one cell thick, putting each cell in contact with any water surrounding the leaves (Rydin and Jeglum, 2013). *Sphagnum* mosses do not have stomata, and so have no active ability to control water loss (Rydin and Jeglum, 2013; Titus et al., 1983). However, one adaptation these mosses have to deal with drought is a high water-holding capacity – as much as 10 -25 times the dry weight of the *Sphagnum* – although this value is different between different species (Andrus, 1986).

6.1.2 Methane fluxes from *Sphagnum*-dominated peatlands

Methane (CH_4) emissions from peatlands covered in *Sphagnum* mosses are often lower than from areas covered in vascular plants (*cf.* (Bowes and Hornibrook, 2006; Greenup et al., 2000; Kip et al., 2010; McNamara et al., 2008; Parmentier et al., 2011; van Winden et al., 2012) (see Table 7.1). Vascular plants with aerenchymous tissues can act as conduits for CH_4 produced in the deeper anoxic layers to pass through to the atmosphere, avoiding the oxic layers above where CH_4 oxidation can occur (Joabsson et al., 1999). As vascular plants have roots that extend down into the anoxic layers in a peatland, their root exudates can also provide substrates for methanogenic archaea (Joabsson et al., 1999). In contrast, *Sphagnum* mosses do not have roots, and so cannot provide substrates to methanogens as quickly as vascular plants can (Clymo, 1970). Also, *Sphagnum* mosses do not have aerenchymous tissue, and so cannot provide direct transport routes for CH_4 out of the deeper peat layers (Rydin and Clymo, 1989). However, another reason cited for lower CH_4 fluxes from *Sphagnum*-dominated areas is the presence of methanotrophs within the plants (Raghoebarsing et al., 2005). Kip et al. (2010) measured CH_4 emissions before and after the removal of *Sphagnum cuspidatum* from nine peat cores. Emissions with the *S. cuspidatum* cover intact were all < 5 mg CH_4 m^{-2} d^{-1}. After removal of the *Sphagnum*, emissions rose to a range of 2-23 mg CH_4 m^{-2} d^{-1}. Using a similar approach, van Winden et al. (2012) found that CH_4 emissions rose significantly ($p < 0.05$) when *S. cuspidatum* cover was removed from mesocosm experiments using peat cores collected from blanket bog at Moor House Nature Reserve. However, often peatlands do not have homogenous vegetation cover, and so comparisons on a species by species level are not always possible. For example, Waddington and Roulet (1996) investigated gaseous fluxes within different topographical features – hollows, hummocks, ridges and pools – each with a distinctive vegetation type and found that although hollow and pools had lower CO_2 and higher CH_4 emissions than hummocks and ridges, the greatest differences were at the microtopographical scale due to the differences in WTP and temperature at this level. Methane fluxes from *Sphagnum*-dominated areas are not always lower than from other vegetation types. For example, Roura-

Carol and Freeman (1999) measured CH_4 fluxes from cores taken from a peatland in the Ogwen Valley, North Wales. The cores had either no vegetation, or were dominated by *Sphagnum recurvum* or *Juncus effusus* (Roura-Carol and Freeman, 1999). The *Sphagnum* cores produced the highest CH_4 fluxes, followed by the *Juncus* cores, and then the cores without vegetation cover (Roura-Carol and Freeman, 1999).

6.1.3 Studies into methanotrophy on peatlands

Table 6.2 shows the approaches that have been taken in studies of methanotrophic activity on peatlands. Each of the studies in Table 6.2 incubated samples, usually in vials and then added CH_4 to the vials. The CH_4 concentrations within the vials were then observed, and any reductions in CH_4 concentrations were attributed to methanotrophy. Hornibrook et al. (2009) attributed the wide range of rates of methanotrophy to the variety of different methods used to measure the process. There are many differences in the methods used in the studies shown in Table 7.2. Some have measured methanotrophy in peat slurries, whilst others have measured methanotrophy within *Sphagnum* mosses. Methanotrophs can reside within *Sphagnum* mosses, and have been shown to occupy the hyaline cells in the lower parts of the plant where no photosynthesis occurs, and also the stem leaves (Basiliko et al., 2004; Raghoebarsing et al., 2005). Raghoebarsing et al. (2005) used a molecular approach to identify where within *S. cuspidatum* plants the methanotrophs resided. Within the hyaline cells of the plant stems, methanotrophs were found in quantities of $10^6 – 10^7$ per plant (Raghoebarsing et al., 2005). Stem leaves housed quantities an order of magnitude smaller at $10^5 – 10^6$ methanotrophs per plant (Raghoebarsing et al., 2005).

Table 6.1: Methane fluxes from peat dominated by different vegetation cover. Positive values indicate release to the atmosphere.

Reference	Field or cores?	Vegetation	CH_4 flux (mg m^{-2} day^{-1})
Bowes and Hornibrook (2006)	Field	*Calluna vulgaris, Eriophorum vaginatum, Trichophorum cespitosum, Molina caerulea* and < 10 % *Sphagnum* spp.	8.9 – 116.1
		75 % *Sphagnum* spp. with *C. vulgaris, E. vaginatum, T. cespitosum, M. caerulea*	-1.5 – 33.9
Greenup et al. (2000)	Field	*E. vaginatum* and *Sphagnum*	75.4 ± 17.2
		Sphagnum spp.	11.9 ± 8.1
Kip et al. (2010)	Cores	Bare peat	0.2 - 23
		Sphagnum cuspidatum	0 - 4.5
McNamara et al. (2008)	Field	*Eriophorum* spp.	52.8 ± 14.4
		Sphagnum spp.	14.4 ± 9.6
		Mixed grasses	2.4 ± 2.4
		C. vulgaris	negligible
Parmentier et al. (2011)	Field	40-90 % cover *Eriophorum angustifolium, Carex aquatilus*	192 ± 980 (mean)
		Sphagnum spp. with 20-30% cover *Eriophorum angustifolium, Carex aquatilus, Comarum palustre*	98.4 ± 74.4 (mean)
van Winden et al. (2012)	Cores	Bare peat	0.0001-0.0011 mg cm^{-2} day^{-1}
		S. cuspidatum	0-0.00065 mg cm^{-2} day^{-1}

Table 6.2 Studies into rates of methanotrophy in peat and *Sphagnum*.

Where given in the literature, species of *Sphagnum* are given in the sample type column. For any *Sphagnum* species listed, '*Sphagnum*' is abbreviated to '*S.*' When species not given in the literature, the entry is listed as '*Sphagnum*'. * indicates samples were washed with deionised water. Positive values indicate methanotrophy, negative values indicate methanogenesis. Any oxidation rates reported as μg g^{-1} were converted to μmol g^{-1} using the following conversion: μg g^{-1} x (1 mol/16.043 g) = μmol g^{-1}. Positive values indicate methanogenesis, negative values indicate methanotrophy

Study	**Sample**		**CH_4**		**CH_4 oxidation rates**
	Type	**Size**	**Max. [CH_4] reached**	**Amount added**	
Basiliko et al. (2004)	*S. magellanicum* *S. majus* *S. fallax* *S. capillifolium* *S. papillosum*	Split into parts (green top, white middle and brown low)	1000 ppmv		Slightly positive to -197 μmol g^{-1} dry weight (DW) d^{-1}
Bellisario et al. (1999)	Peat slurries	5 g wet weight	10000 ppmv		-0.25 to -3.6 μmol g^{-1} d^{-1}
Frenzel and Karofeld (2000)	Peat	1-2 g dry weight	1400-18000 ppm		None detected
Kip et al. (2010)	*Sphagnum** including *S. magellanicum* *S. cuspidatum*	Intact mosses		1 ml pure CH_4	0 to -80 μmol g^{-1} DW d^{-1}

Study	**Sample**		**CH_4**		**CH_4 oxidation rates**
	Type	**Size**	**Max. [CH_4] reached**	**Amount added**	
Larmola et al. (2010)	*Sphagnum** 23 species incl. *S. cuspidatum*	30 g	10000 ppm		0 to -62 µmol g^{-1} DW d^{-1}
McDonald et al. (1996)	Peat slurries	30 ml	0.1 % v/v C_2H_2 2 % v/v		~-2 to -35 µmol g^{-1} DW d^{-1}
Moore and Dalva (1997)	Peat	5 g wet weight		800-1000 µl	-0.82 µmol g^{-1} d^{-1} (mean)
Parmentier et al. (2011)	*Sphagnum** incl. *S. balticum* *S. compactum* *S. subsecundum* *S. squarrosum*	Whole plants 20 g wet weight		1 ml pure CH_4	-30 to -80 µmol g^{-1} DW d^{-1}
Putkinen et al. (2012)	*S. magellanicum* *S. majus*	30 ml, only upper 10 cm of plants	10000 ppm		0 to -18 µmol g^{-1} DW d^{-1}
Raghoebarsing et al. (2005)	*S. cuspidatum** *S. magellanicum** *S. papillosum**	6 g		1 ml pure CH_4	~-1 to -29 µmol g^{-1} DW d^{-1}

Study	**Sample**		**CH_4**		**CH_4 oxidation rates**
	Type	**Size**	**Max. [CH_4] reached**	**Amount added**	
Rinnan et al. (2003)	Peat at 10-15 cm depth	30 ml	1 %		-48 to -72 µmol g^{-1} d^{-1}
Sundh et al. (1995)	Peat slurries	10 g	Not stated		0 to -7 µmol g^{-1} wet peat d^{-1}
van Winden et al. (2012)	*S. capillifolium** *S. cuspidatum**	Split into parts (top, middle, bottom, 3 cm each)		1 ml	~-0.16 to -0.66 µmol g^{-1} DW d^{-1}

Many of the studies in Table 6.2 differed in whether they reported the amount of CH_4 supplied to the peat or *Sphagnum* samples, or the maximum CH_4 concentration reached within the vial or flask the sample was housed in for the experiment. A common maximum CH_4 concentration was 10000 ppm, although Basiliko et al. (2004) used a much lower concentration of 1000 ppm. Basiliko et al. (2004) chose this CH_4 concentration because it was similar to concentrations recorded by Blodau and Moore (2003) in cores from the Mer Bleue peatland in Ontario, Canada, which is also where the study by Basiliko et al. (2004) was based. Basiliko et al. (2004) also measured CH_4 concentrations just below *Sphagnum* capitula *in situ* across a range of peatland topographical features and found that, with the exception of a pond area, CH_4 concentrations were < 10 ppm.

There are two different types of methanotrophic activity: high affinity and low affinity (Lai, 2009; Segers, 1998). High-affinity methanotrophy occurs when CH_4 concentrations are close to ambient, and low-affinity methanotrophy occurs at CH_4 concentrations higher than ambient (Lai, 2009; Segers, 1998). Therefore, all of the studies in Table 6.2 were testing for the activities of low-affinity methanotrophs, because the majority used CH_4 concentrations significantly higher than ambient concentrations (approximately 2 ppm).

Parmentier et al. (2011) highlighted that the most common units used in reporting CH_4 oxidation rates are μmol CH_4 g^{-1} dry weight day^{-1}, whereas CH_4 fluxes are most commonly reported as mg CH_4 m^{-2} day^{-1}, which can make comparisons of the two rates problematic. Some of the oxidation rates reported in Table 6.2 were originally in units of μg CH_4 g^{-1} day^{-1}, but were converted to μmol CH_4 g^{-1} day^{-1} to allow for a better comparison between studies.

McDonald et al. (1996) did not only add CH_4 to the peat slurry samples, but also used a methanotrophic inhibitor, acetylene (C_2H_2), to determine rates of

methanotrophy. Acetylene inhibits the ability of the enzyme methane monooxygenase (Prior and Dalton, 1985), which is responsible for the initial oxidising reaction between methanotrophs and CH_4 (Colby and Dalton, 1976). McDonald et al. (1996) used C_2H_2 to ascertain that the loss of CH_4 from their incubations was due to methanotrophic activity. After the injection of C_2H_2, the decline in CH_4 concentrations stopped and concentrations remained constant, indicating that methanotrophic activity had been occurring (McDonald et al., 1996). Kip et al. (2010) also used C_2H_2 to determine that the methanotrophy observed was indeed microbial activity, and not any other form of loss from the experimental system.

6.1.4 Methanotrophy and *Sphagnum*: a mutually-beneficial relationship?

The relationship between *Sphagnum* and methanotrophs is mutually beneficial; the oxygen (O_2) produced during photosynthesis can be used by the methanotrophs to oxidise CH_4, and the carbon dioxide (CO_2) produced during methanotrophy can be used by the *Sphagnum* for photosynthesis (Putkinen et al., 2012). Kip et al. (2010) suggested that this relationship is not as strong when *Sphagnum* is not submerged, because the supply of atmospheric CO_2 is sufficient for the plants to photosynthesise, and so the *Sphagnum* is just a host for the methanotrophs. Gaseous diffusion through water is much slower than in air (Haynes, 2012), and so the more-accessible supply of CO_2 as a result of methanotrophy benefits the *Sphagnum* mosses (Kip et al., 2010). Also, during submergence there is less O_2; however, the photosynthesis provides a supply O_2 for the methanotrophs (Putkinen et al., 2012). Kip et al. (2010) studied this symbiosis with *S. magellanicum* from a Canadian peat bog pool using $^{13}CO_2$ and $^{13}CH_4$. Approximately 35 % of the CO_2 taken up by the *S. magellanicum* was found to originate from the CH_4 (Kip et al., 2010). Larmola et al. (2010) and Raghoebarsing et al. (2005) reported that 10-30 % of *Sphagnum* biomass carbon was sourced from CH_4 oxidation. Through both a *Sphagnum* transplantation experiment and a

Sphagnum bathing experiment, Putkinen et al. (2012) found that methanotrophs could be transported in water, so the symbiosis between methanotrophs and *Sphagnum* may not be as strong as other literature suggests (Putkinen et al., 2012). This finding suggested that methanotrophic activity within *Sphagnum* would be more resistant to drought, because if methanotrophs can be transported through water, then if a methanotrophic community suffered due to the effects of drought within their host Sphagnum mosses, new methanotrophs could re-colonise the plant (Putkinen et al., 2012).

Some studies have found this symbiotic relationship to be most effective where the *Sphagnum* is submerged (Raghoebarsing et al., 2005; Basiliko et al., 2004; Kip et al., 2010). Kip et al. (2010) found that *Sphagnum magellanicum* with capitula situated 5 - >20 cm above the water level had average CH_4 oxidation rates of 0-0.01 µmol g^{-1} dry weight day^{-1} at both 10 °C and 20 °C. However, *S. magellanicum* with the capitula situated only 0-5 cm above the water table had average CH_4 oxidation rates of 5-10 µmol g^{-1} dry weight day^{-1} at 10 °C, with the average rate increasing to 12-23 µmol g^{-1} dry weight day^{-1} at 20 °C (Kip et al., 2010). This increased average rate of CH_4 oxidation at a higher temperature also highlights the relationship between methanotrophic bacteria and temperature. Raghoebarsing et al. (2005) studied the methanotrophy potential of *Sphagnum* mosses by section and submergence. The different parts of the *Sphagnum* mosses were the top 10 cm, middle 10 cm and lower 10 cm. There was submerged *S. cuspidatum* in pools, and non-submerged *Sphagnum magellanicum* and *Sphagnum papillosum* in lawns. The difference, if any, between *S. magellanicum* and *S. papillosum* is not detailed in the study; they are classed together as lawn species. The submerged *S. cuspidatum* showed consistently higher rates of potential methanotrophy than the non-submerged *Sphagnum* species in all parts of the plants. For the *S. cuspidatum*, the middle parts of the plant had the highest methanotrophic potential (~28 µmol CH_4 g^{-1} dry weight day^{-1}), followed by the top parts (~20 µmol CH_4 g^{-1} dry weight day^{-1}) and then the lower parts (~17 µmol CH_4 g^{-1} dry weight day^{-1}) . The lower parts of the *S. magellanicum* and *S. papillosum* had the highest methanotrophic potential

(~7 µmol CH_4 g^{-1} dry weight day^{-1}), and the top and middle parts had similar potentials to each other (~1 µmol CH_4 g^{-1} dry weight day^{-1}) (Raghoebarsing et al., 2005).

6.1.5 Photosynthesis and drought within *Sphagnum* mosses

Photosynthesis is a key part of the symbiotic relationship between methanotrophs and the *Sphagnum* in which they can reside. Basiliko et al. (2004) studied CH_4 oxidation potential in *Sphagnum* mosses that had been separated into three parts based on their colour, and hence photosynthetic ability: green (top), white (middle) and brown (lower). The photosynthetic top sections had the lowest rates of CH_4 oxidation in all five of the species investigated (listed in Table 6.2), although these rates were only significantly different from the lower brown parts in *Sphagnum fallax* and *Sphagnum majus* (Basiliko et al., 2004).

Moisture content is a major control of the photosynthetic abilities of *Sphagnum* mosses (Tuittila et al., 2004; Williams and Flanagan, 1996). If moisture is lacking then metabolic processes become restricted; however, too much water slows down gaseous diffusion rates and restricts CO_2 fixation (Tuittila et al., 2004; Williams and Flanagan, 1996). Drought can damage the photosynthetic abilities of *Sphagnum* (Harris, 2008), although the exact definition of drought or the duration thereof is not defined. During periods of drought plants can absorb an excessive amount of light; more than they require for photosynthesis (Demmig-Adams and Adams, 1992), and it is this surplus of energy that can damage the photosynthetic abilities (Demmig-Adams and Adams, 1992; Harris, 2008). If there are repeated cycles of drought, photosynthesis may never recover (Schipperges and Rydin, 1998). Within *Sphagnum* mosses, the chlorophyllose cells that carry out the photosynthetic functions are located in between the hyaline cells (Rinnan and Holopainen, 2004). Gerdol et al. (1996) found damage to the chlorophyllose cells

in *Sphagnum fallax*, *Sphagnum magellanicum* and *Sphagnum capillifolium* after a controlled drying experiment. If *Sphagnum* mosses suffer drought, but are then submerged in response to a rising WTP, it is unclear if this also has an effect on methanotrophy. The supply of O_2 from photosynthesis is no longer available for the methanotrophs to aid their consumption of CH_4; therefore, reduced levels of methanotrophy should be expected due to the lack of O_2. When the WTP is re-established, if the photosynthetic abilities of the Sphagnum plant have not been damaged, then renewed levels of methanotrophy would be expected. However, Putkinen *et al.* (2012) found that methanotrophs could be dispersed by water, so if methanotrophs die when the O_2 supply is reduced, methanotrophic activity could be reestablished through the transfer of new methanotrophs to the *Sphagnum* mosses when the WTP is reestablished. As yet no literature has been found to suggest if hyaline cells are also damaged during drought. If hyaline cells are damaged, there may be a knock-on effect to the methanotrophs living within the cells, which could affect the ability of the methanotrophs to function. Therefore, the effects that drought may have on the symbiosis between methanotrophs and *Sphagnum* are unclear.

Therefore, to address these research gaps, a controlled laboratory mesocosm experiment was designed to assess the effects of drought and re-submergence on *Sphagnum cuspidatum* plants, through subjected sub-samples to various treatments of drought and submergence, and monitoring the effects thereof on methanotrophic activity. The results of this experiment should aid peatland managers in the understanding of the effects of a lower WTP on methanotrophy compared to a higher WTP. Climate can affect the efforts of peatland managers to maintain a high WTP (close to the peat surface), and so a greater understanding of the response of methanotrophs to different moisture conditions is important for carbon storage.

6.1.6 Aim

Through an experiment designed to test for the effects of drought and submergence on the methanotrophic potential of *Sphagnum cuspidatum*, this study will address research questions 5 and 6.

5. **Does drought affect methanotrophic activity within *Sphagnum* mosses?**
6. **Does submergence affect methanotrophic activity within *Sphagnum* mosses that have been subjected to drought?**

6.2 Methodology

In brief, to address research questions 5 and 6, an experiment was designed whereby sub-samples of *S. cuspidatum* were subjected to different treatment combinations of drought and submergence. Following incubations in these treatment conditions, each *Sphagnum* sub-sample was sealed into a flux chamber where CH_4 concentrations could be monitored. Half of the sub-samples, once sealed in the flux chamber, were given a dose of CH_4 so the rate of CH_4 concentration change in the chamber could be used to calculate any potential methanotrophy. So that they could act as controls, the other half of the sub-samples were not given any CH_4; by having this control it was possible to assess if any methanogenesis was occurring that could potentially blur the signal detected (if any) in the treatments where CH_4 was added. The results were then analysed to see if there were any statistically significant differences between the rates of methanotrophy from the different treatments.

6.2.1 Sample collection

The dominant type of *Sphagnum* at both Thorne and Hatfield Moors is *S. cuspidatum* (T. Kohler, pers. comm.), and this species is also dominant at many restored peatlands. This species of *Sphagnum* has also been the subject of several

of the studies listed in Table 6.2. Therefore, it was chosen as the *Sphagnum* species to use for this experiment.

Sample collection took place on Thorne Moors from an area where restoration began in 2005 (Lat. 53.657788 N, Long. -0.90813980 W). Samples were collected from Thorne Moors rather than Hatfield Moor because water-table positions at Thorne Moors have been much more stable. Therefore, the *Sphagnum* collected is much less likely to have suffered from drought in the past, which could have an impact on the results. If the plants have been subjected to previous wet and dry cycles, the photosynthetic functions of the plant tissues may be damaged (Proctor, 1982; Williams and Flanagan, 1996). Figure 6.1 shows the area from which the samples were collected: the edges of an area of surface inundation. *Sphagnum cuspidatum* was growing both on the peat surface under the open water and around the edges of the open water within the *Eriophorum* (mostly *Eriophorum angustifolium* with some *Eriophorum vaginatum*).

Sample collection was completed in two phases. On 23/01/2014, 60 litres of water (from here on referred to as field water) was collected. Field water was used both here and later during incubations to simulate field conditions as much as possible. In many of the studies noted in Table 6.2 *Sphagnum* samples were washed with deionised water prior to the experiments, but no reasons for this choice were given, which reinforced the decision to use field water in this experiment. *Sphagnum cuspidatum* was collected on 18/02/2014. The pH, dissolved oxygen concentration and conductivity of the surface water were analysed *in situ* on both occasions, as shown in Table 6.3. Within 24 hours of collection, ten random samples of field water were prepared for analysis of their dissolved organic carbon (DOC) concentrations. These samples were analysed within five days of filtration, and an average of the data is also shown in Table 6.3.

Once back in the laboratory the field water was kept in a fridge at 4 °C. The *S. cuspidatum* was housed in shallow trays, partially filled with water collected at the same time as the *S. cuspidatum*. The trays were located in the laboratory, and so were able to acclimatise to indoor ambient temperatures. Water levels were regularly maintained with field water, and the *S. cuspidatum* was regularly sprayed with field water to keep the capitula moist.

Figure 6.1: Area from which *Sphagnum cuspidatum* samples were collected

Table 6.3: Water chemistry of the area from which *Sphagnum* samples were collected

Date		pH	Dissolved oxygen (mg L^{-1})	Conductivity (µs cm^{-1})	DOC (mg L^{-1})
23/01	***n***	3	3	3	10
	Average	3.3	11.7	127.6	131.6
18/02	***n***	3	3	3	n/a
	Average	4.0	10.5	113.1	

6.2.2 Experimental design

6.2.2.1 Treatments and sub-sample preparation

In order to assess the various combinations of drought and submergence that *Sphagnum* could be subjected to, 96 sub-samples of *S. cuspidatum* were required for this experiment. Half of these sub-samples (48) were incubated for seven days, and the other half for 28 days. The purpose of the two different incubation times was to assess if length of treatment exposure had any effect on the results. There were four combinations of drought and submergence, as shown in Table 6.4, and these four combinations were replicated to give eight treatments to allow for a set of four duplicate treatments to act as controls where no CH_4 was given to the sub-samples after incubation. Each treatment had six replicates, and therefore a total of 48 sub-samples per incubation time period.

Sub-samples were defined by their wet weight: 40 ±0.5 g. Seven days prior to the incubation start date, the sub-samples that needed to be dried were prepared. Pre-experiment tests had determined that seven days was sufficient time to dry out the defined sub-sample weight. To prepare the sub-samples, individual *Sphagnum* plants were measured out until the correct weight per sub-sample was

reached and left to air dry. Sub-samples that were to remain wet were weighed out no more than three hours prior to the incubation start.

Table 6.4: Experiment treatments and identification numbers. Six replicates per treatment

***Sphagnum* treatment**	**CH_4 added**		**control – no CH_4 added**	
	dried	**wet**	**dried**	**wet**
submerged	2	5	4	8
not submerged	3	6	7	1

6.2.2.2 Incubation conditions

Many of the studies cited in Table 6.2 have conducted experiments to assess the CH_4 oxidation potential of *Sphagnum* samples using an incubation method with no light. However, because a method with no light removes the effects of photosynthesis, that method could not be adopted for this study. Instead, an environmental cabinet (Weiss-Gallenkamp Fitotron SGC097.CPX.F growth chamber) was used, where diurnal cycles of light and temperature could be programmed. The use of this environmental cabinet allowed for a more realistic system for the samples to be housed in during the experiments. The *Sphagnum* samples were collected in winter due to time constraints; however, light, humidity and temperature regimes within the cabinet were set to reflect conditions during routine sampling in August 2012, as shown in Table 6.5. This time period was chosen because it was when CH_4 fluxes to the atmosphere were at their highest. The CH_4 concentrations within the environmental cabinet during the incubations were at ambient levels. Measurements near the end of the 28-day incubation showed CH_4 concentrations between 2.1 and 2.3 ppm.

Table 6.5: Settings for the environmental cabinet

	Daytime setting	Night-time setting
Setting duration	15 hours	9 hours
Light intensity	552 – 784 µmol m^{-2} s^{-1}	0 µmol m^{-2} s^{-1}
Temperature	17.8 °C	12.9 °C
Humidity	80.6 %	94 %

The PAR levels across the cabinet were very variable. The reason for the large variability could not be found; however, every effort was taken to reduce the effect of the variation. Table 6.6 shows the exact location and values of each reading. The location for each reading was defined by the container placement for the sub-samples. The two blacked-out squares are where the PAR levels were lowest within the cabinet. It was possible to fit all of the sub-samples in the cabinet without using these two locations. To try and achieve equal PAR exposure across all replicates in all treatments six blocks of eight locations were created. The first block contained the locations of the eight lowest PAR levels; the second block contained the locations of the next eight PAR levels and so on. One replicate from each treatment was assigned to each block. As much as possible within the experiment design was randomised: treatment number, sub-sample numbering, input regime and cabinet placement. Table 6.6 also shows the final cabinet placement plan. The resulting average PAR levels across each treatment were between -9 and 6 µmol m^{-2} s^{-1} of the average level of the cabinet as a whole, as shown in Table 6.7

Figure 6.2 shows the containers in which the sub-samples were placed for their incubation in the environment cabinet. The containers were made from plastic

(Lock & Lock) (Figure 6.2d). Each container had a small shelf placed inside for the *S. cuspidatum* to rest on. The shelves were made from the bases of smaller plastic containers (Wilkinsons), with 32 holes drilled into each one to allow for water to pass through (Figure 6.2a). The stand for each shelf was made from nylon pipe. For the submerged sub-samples, the stand was 1.25 cm high and had 10 holes that allowed the passage of water (Figure 6.2c), and for the sub-samples that were not submerged, the stand was 2.5 cm high and had 20 holes (Figure 6.2b). Each stand and shelf was fixed together and to the base of the incubation container using Blu-tac.

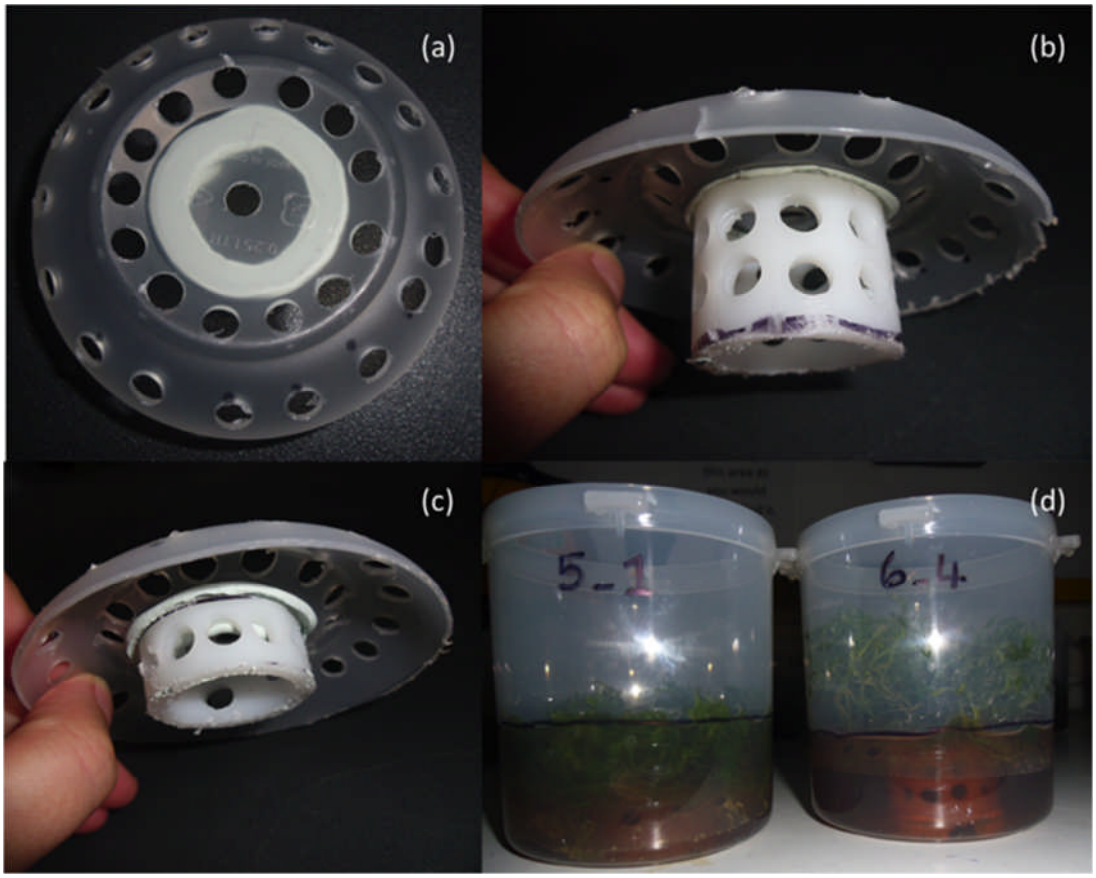

Figure 6.2: Photographs of incubation containers and parts: (a) shelf for sub-samples to sit on in container; (b) stand and shelf for sub-samples not submerged; (c) stand and shelf for submerged sub-samples; (d) an example of submerged (left) and not submerged (right) sub-samples in containers

Table 6.6: Plan-view of the PAR (µmol m^{-2} s^{-1}) levels prior to 7-day incubation and sub-sample placement across the environmental cabinet. Colours refer to different PAR blocks'. The upper number in each box is the PAR level, and the lower number denotes the treatment_replicate sub-sample ID in that position.

596 1_1	647 5_2	675 7_3	694 2_4	681 8_4	665 5_3	622 4_2	569 3_1	
664 6_2	720 4_5	738 5_5	750 3_6	741 7_5	721 6_5	680 5_4	635 1_2	
685 6_4	725 8_5	766 1_6	784 6_6	775 5_6	753 7_6	717 1_5	673 1_3	
667 2_3	711 1_4	746 8_6	760 2_6	766 4_6	730 3_5	712 2_5	671 4_3	
639 8_2	652 3_2	672 6_3	687 4_4	694 7_4	705 3_4	673 8_3	673 3_3	
596 4_1	622 2_2	631 7_2	608 8_1	552 5_1	578 6_1	579 7_1	558 2_1	

Table 6.7: PAR levels (µmol m^{-2} s^{-1}) within the environment cabinet

Treatment	Average PAR levels per treatment	Difference with whole cabinet average
1	683	5
2	669	-9
3	680	2
4	677	-1
5	676	-2
6	684	6
7	679	1
8	679	1
Whole cabinet	678	n/a

6.2.3 Flux measurements

6.2.3.1 Chamber design

In order to accurately measure the change in CH_4 concentration in the sub-samples after their incubations, a chamber was needed that could be connected to a gas analyser allowing constant monitoring of CH_4 concentration change over time. For the treatments where CH_4 was added, the chamber also needed to allow for CH_4 to be injected into the chamber whilst keeping the gas-tight seal intact. A small vacuum desiccator made from borosilicate glass (10 cm I.D. x 17.4 cm, 895 ml volume, Duran) was used as a chamber to measure the change in CH_4 concentration (from here on referred to as chamber), as shown in Figure 6.3. The chamber lid had a 2.4 cm hole in the top, into which a polyvinyl chloride (PVC) bung was placed. The bung had three holes drilled through it, two of 0.4 cm and one of 1 cm diameter. Three glass tubes were fitted through the holes; each cut to a different length. The two tubes of the smaller diameter were cut to 6.5 and 9 cm

respectively, and the wider tube was cut to 8 cm. The wider tube was for a Suba-seal septum to allow for CH_4 to be injected into the chamber once sealed. Each of the remaining glass tubes had Tygon tubing fitted over them, the opposite ends of which then fitted into a gas analyser (see section 7.2.3.2). In order to allow for airflow around the samples a shelf was placed into the chamber. The shelf was made and fixed in place in exactly the same way as described in Section 7.2.2.2 for the incubation containers, with the addition of an extra piece of 2.5 cm pipe to the stand, making a full stand height of 5 cm. To create a gas-tight environment, petroleum jelly was spread around the ground-glass surfaces on both the chamber base and lid. Upon bringing the two surfaces together, the lid was twisted to smear the petroleum jelly and create a gas-tight seal. The sides of the PVC bung were also coated in petroleum jelly, and when the bung was placed into the hole in the chamber lid, it was twisted to smear the petroleum jelly and create a gas-tight seal. Petroleum jelly was also smeared around the joins between the bung and the hole in the lid, and between the three glass tubes and the bung. The septum was replaced whenever it contained visible perforations.

Figure 6.3: Photograph of the chamber used, including an inset photograph of the PVC bung.

6.2.3.2 Measuring gaseous concentrations

A Los Gatos Research Ultraportable Greenhouse Gas Analyser (LGR_UGGA) was used to measure concentrations of CH_4 in the chamber (accuracy: > 99 %, precision: 2 ppb). The instrument also records concentrations of CO_2 (accuracy: > 99 %, precision: 300 ppb).

Upon removal from the environmental cabinet after the corresponding incubation period, each *S. cuspidatum* sub-sample was photographed. The sub-sample was then lifted from its container, and after the free water had drained, the sub-sample was weighed. The sub-sample was then placed onto the shelf in the chamber, and the air temperature and barometric pressure in the room were recorded (C4141 Commeter probe). The chamber was then sealed, with the lid placed on slowly in order to not trap any extra air and over-pressurise the chamber system. If the

treatment to which the sub-sample belonged required CH_4 input, then 1.9 ml of air was removed from the chamber via the septum in the chamber lid. Then 1.9 ml of 10000 ppm CH_4 was injected. Both air removal and CH_4 injection with the syringe were done slowly so as not to over-pressurise the chamber system. Immediately after the CH_4 was added, the syringe was slowly pumped up and down five times in order to gently mix the air within the chamber. The addition of this volume of CH_4 raised the concentrations within the chamber to a maximum of approximately 20 ppm. This concentration was chosen based on the results of Basiliko et al. (2004), where *in situ* CH_4 concentrations were measured below *Sphagnum* capitula. With the exception of a pond, all CH_4 concentrations were < 10 ppm, so because the *Sphagnum* mosses used had stems as well as capitula, a concentration double that found below the capitula was deemed appropriate.

Each chamber test ran for 2300 seconds from the time the chamber was sealed to allow for CH_4 to be added, mixed using the syringe and to reach peak concentration, after which there would still be 1800 seconds of data to use for flux calculations. After the chamber test, the sub-sample was removed from the chamber and placed in a pre-weighed evaporating basin. Sub-samples were left to air-dry for approximately 24 hours, and were then placed in an oven at 80 °C for 24 hours to ascertain the dry weight of the sub-sample.

6.2.4 Flux calculations

6.2.4.1 Calculating rates of methanotrophy and methanogenesis

The output from the LGR_UPGHGA gave a reading of CH_4 concentrations within the chambers every second. The first 500 seconds of every test were discarded to make sure that the readings used to calculate fluxes were of well-mixed air within the chamber. All flux calculations were based on 1800 seconds of data, and the methods of flux calculation were adaptations of the method described in Section 3.2.2.3. Unlike in earlier chapters, these flux calculations were not based on linear regression. From the data remaining after the removal of the first 500 seconds, the

maximum CH_4 concentration was identified. An average was calculated using the 20 seconds before and after the maximum concentration. Similarly, at the 1800 second CH_4 concentration (1800 seconds after the maximum CH_4 concentration), an average was calculated in the same way. The two resulting CH_4 concentrations from these two averages were taken forward to the flux calculations, where they were converted into mass of CH_4, as described in Section 3.2.2.3. The following equation was applied to obtain a flux:

$$\frac{\Delta \mathrm{CH_4} - \left(P \times \mathrm{CH_{4,t_1}}\right)}{A_s} \times \frac{86400}{t_2 - t_1} \qquad \textbf{Equation 6.1}$$

where t_1 = test start time (s), t_2 = test end time (s), $\Delta\ \mathrm{CH_4}$ = change in CH_4 mass (mg) between t_1 and t_2, P = proportion of CH_4 mass lost from chamber set-up (explained below in Section 6.2.4.2), $\mathrm{CH_{4,t1}}$ = CH_4 mass at t_1 and A_s = area occupied by *Sphagnum* sub-sample (explained below in this section).

The flux calculation method requires an area on which to base the resulting flux; so, for the fluxes reported earlier in Chapter 4, this area was the area occupied by the collar upon which the flux chamber was placed in order to report fluxes of mg CH_4 m^{-2} day^{-1}. There were two options for this experiment for the convention to use for fluxes. The first, to report fluxes as mg CH_4 m^{-2} day^{-1} for comparison against fluxes from field measurements, needed the area occupied by the mass of *Sphagnum* used for each sub-sample in the field. However, the second option was chosen; to report fluxes as µmol g^{-1} dry weight (DW) day^{-1} to allow for comparison against similar experiments reported in the literature. Therefore, fluxes were first calculated as mg CH_4 g^{-1} DW day^{-1}, using the dry weight of the sub-sample in place of the area on which to base the flux. Then the following conversion was applied:

mg g^{-1} DW day^{-1} x 1000 = µg g^{-1} DW day^{-1} x (1 mol/16.043 g) = µmol g^{-1} DW day^{-1}

6.2.4.2 Accounting for losses

Prior to the start of the experiment, the chamber set-up was tested for leaks, to ensure that a gas-tight environment had been created. Leak tests were conducted by setting up a blank (empty) chamber test, adding CH_4 and monitoring the concentration change over time (as described in further detail below). Unfortunately, a small leak in the system was detected and could not be specifically identified or rectified. Therefore, the loss of CH_4 mass from the system over 1800s (P in Equation 6.1) was quantified from five blank chamber tests so that it could be accounted for in the experimental results, and not mistaken for methanotrophic activity. From the results of these five blank chamber tests, the highest (0.0164) and lowest (0.01) proportion losses were taken forward into the flux calculations. Therefore, each sub-sample had two fluxes calculated on a dry-weight basis: a lower proportion loss and a higher proportion loss.

Given that there was water held within the *Sphagnum* mosses that did not freely drain prior to the chamber tests, CH_4 concentrations within the chamber could also have declined due to CH_4 dissolving into this water. The amount of CH_4 that could have passed into solution under equilibrium conditions was calculated in order to quantify this potential loss. A method pre-defined for the Defra SP1202 project[1] was used, whereby the partitioning of gas between a gaseous and aqueous phase was calculated. An empirical equation from Fogg and Gerrard (1991) was used to estimate solubility under standard temperature and pressure, and used Henry's Law to adjust for ambient temperature and pressure. When applied to the chamber set-up for this experiment, the results suggested that a proportion as great as 0.005 of the added CH_4 could pass into solution. This value can be considered as a worst-case scenario because it applies to an equilibrium condition; the time taken for gas to pass into solution is not allowed for. Equilibrium may

[1] For more information please see http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=16991

take longer than the 1800 seconds during which measurements occurred. In order to test the validity of this result for the chamber conditions, further blank chamber tests were conducted, two exactly as described above and two with the addition of 95 ml of deionised water. All but one of the 96 sub-samples held less than this amount of water during the chamber tests, which again makes the results a worst-case scenario in terms of how much CH_4 could have passed into solution. The results of these additional blank chamber tests showed that a proportion of 0.0043 of the CH_4 added passed into solution over the 1800 seconds used to calculate a flux. Therefore, this 0.0043 proportion was used instead of the 0.005 proportion described above to represent this particular loss. The 0.0043 proportion was added to the higher and lower proportional losses described above, which resulted in final proportion losses of 0.0207 and 0.0143 respectively. All other losses detected were attributed to methanotrophic activity. The final methanotrophic rates reported are likely to be conservative, because any methanogenic rates found in the control sub-samples could not be accounted for, due to different sub-samples being used for methanogenesis and methanotrophic flux tests.

6.2.5 Statistical analyses

To address research questions 5 and 6, the data from this experiment were analysed using the following methods. Bivariate linear regression was used on a per-treatment basis (n = 6 replicates per treatment) to determine if the different levels of PAR across the environmental cabinet had any effect on the CH_4 fluxes, using Microsoft Excel 2010. To examine the differences between the fluxes from the different treatments, factorial ANOVA tests were applied separately to the results from the CH_4 addition results and the control sample results using SPSS. The three factors were level of drought (dried, wet), level of submergence (submerged, not submerged) and incubation period (7-day, 28-day).

6.3 Results

6.3.1 Post-incubation conditions of the sub-samples

Figure 6.4 shows the pre- and post-incubation conditions of one sub-sample per main treatment type. The particular sub-samples chosen for Figure 6.4 were selected in order to highlight some of the conditions that developed within certain sub-samples during incubation. Figure 6.4a shows that some sub-samples that were dried and not submerged developed mould growth during their incubation in the environment cabinet (white growth on some leaves). The particular sub-sample in Figure 6.4a was the worst case. Some sub-samples from the dried and submerged treatment developed algae growth during incubation, which in Figure 6.4b can been seen as a green film on the water surface in the post-incubation photograph. Both the mould and algal growths were attributed to weakened defences through drying of the *Sphagnum* plants and the non-natural conditions to fight these growths. Many sub-samples in all treatments displayed blackened tips on the leaves, an example of which can be seen in Figure 6.4c. As evaporation occurred throughout the incubation process, solutes collected on the leaf tips, causing the black colouring observed. Although not shown in Figure 6.4, some sub-samples also developed signs of chlorosis, with areas of yellowed capitula developing in patches.

Some sub-samples grew during incubation, which slightly changed the nature of their incubation conditions. Unsurprisingly it was the wet and submerged sub-samples that displayed growth, which meant that at the end of the incubations, these sub-samples were no longer submerged (Figure 6.4d). Original water levels within each sub-sample container were maintained daily throughout the incubations; however, to have given some sub-samples more water than others would have changed the nature of the experiment. Therefore, these sub-samples were allowed to grow above the maintained water level.

Figure 6.4: Photographs of selected sub-samples pre- (left) and post-incubation (right) for each of the four main treatment types: (a) = dried, not submerged (3_1); (b) = dried, submerged (2_1); (c) = wet, not submerged (1_2); (d) = wet, submerged (5_4). Brackets indicate which treatment_sub-sample the photographs are of. All sub-samples shown from the 28-day incubation period.

6.3.2 Differences in flux calculation methods

Figure 6.5 shows the differences in fluxes that can occur depending on the different methods used to calculate the flux. The data shown in Figure 6.5 are from the six replicates of the 7-day incubation of treatment 3, which was dried and not submerged, and had CH_4 added during the post-incubation chamber test. The results of the other seven treatments, and from both incubation durations, all showed a similar pattern to the results in Figure 6.5 when the results were expressed in µmol CH_4 g^{-1} DW day^{-1}. The lower proportional loss calculation always had the lowest flux (highest rates of methanotrophy) and so were the best-case scenario, and the higher proportional loss calculation always had the highest flux (lowest rates of methanotrophy) and so were the worst-case scenario. For the treatments where no CH_4 was added in the chamber tests, the fluxes from the low area calculations were always higher (more methanogenesis) than the fluxes from the high area calculations.

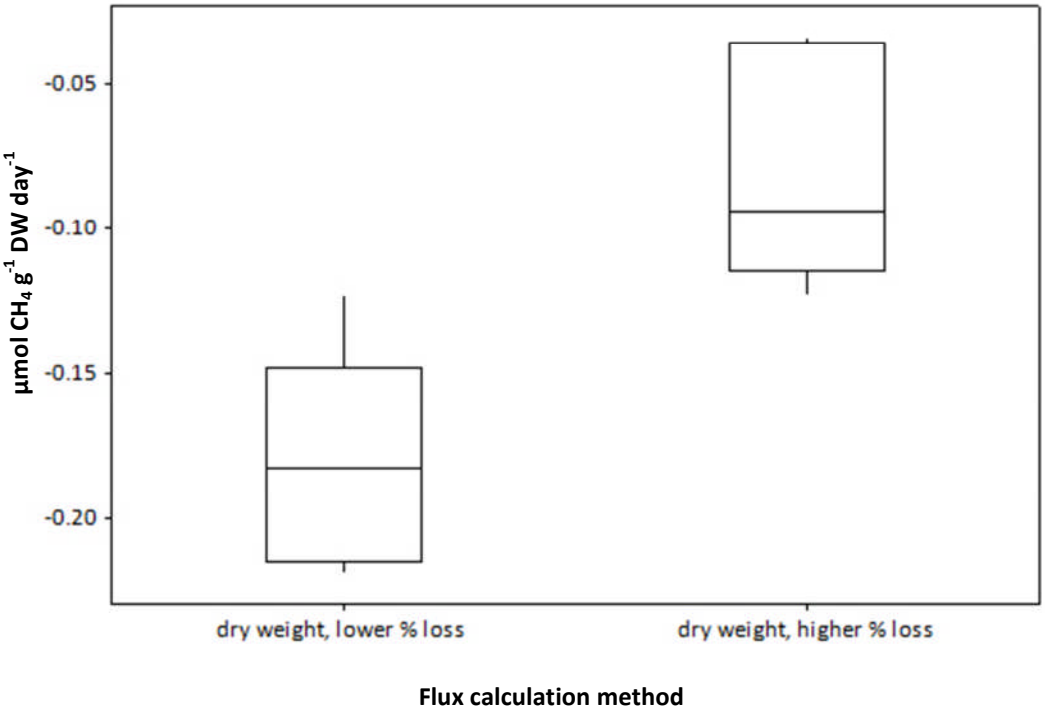

Figure 6.5: The differences in results from the different methods of flux calculation for the 7-day treatment 3. Negative values indicate methanotrophy. Plotting convention as in Figure 4.2

Unless otherwise stated, any further results shown graphically and any statistical results for any treatment will be from the lower proportional loss calculations for the specific treatment and incubation period in question. It is recognised that expressing the results in these formats are the best-case scenarios and therefore may be an overestimation of the rates of methanotrophy.

6.3.3 Effects of incubation period and treatment type

To address research questions 5 and 6, factorial ANOVA was applied to the data shown in Figure 6.6; the fluxes measured from the six sub-samples within each of the eight treatments for both the 28-day and 7-day incubations. The three factors were level of drought (dried or wet), level of submergence (submerged, not submerged) and incubation period (7-day or 28-day). Data from Figure 6.6a were analysed separately from the data in Figure 6.6b. There were no significant differences between any of the treatments shown in Figure 6.6a (p = 0.06-0.47), which indicates that none of the three factors (alone or combined) had an effect on the abilities of methanotrophs to oxidise CH_4. From the data in Figure 6.6b, there was a significant difference between the two levels of drought (p = 0.001) across both submergence levels and incubation periods. From visual analysis of the data in Figure 6.6b, this significant difference indicates that the wet treatments had significantly lower rates of methanogenesis than the dried treatments. There were no other significant differences (p = 0.052-0.57) between any of the other factors (alone or combined) for the data in Figure 6.6b, indicating that level of submergence and incubation period had no effect on the abilities of methanogens to produce CH_4. The lack of further significant differences also indicates that the level of drought in combination with either level of submergence or incubation period had no significant effect on the methanogens.

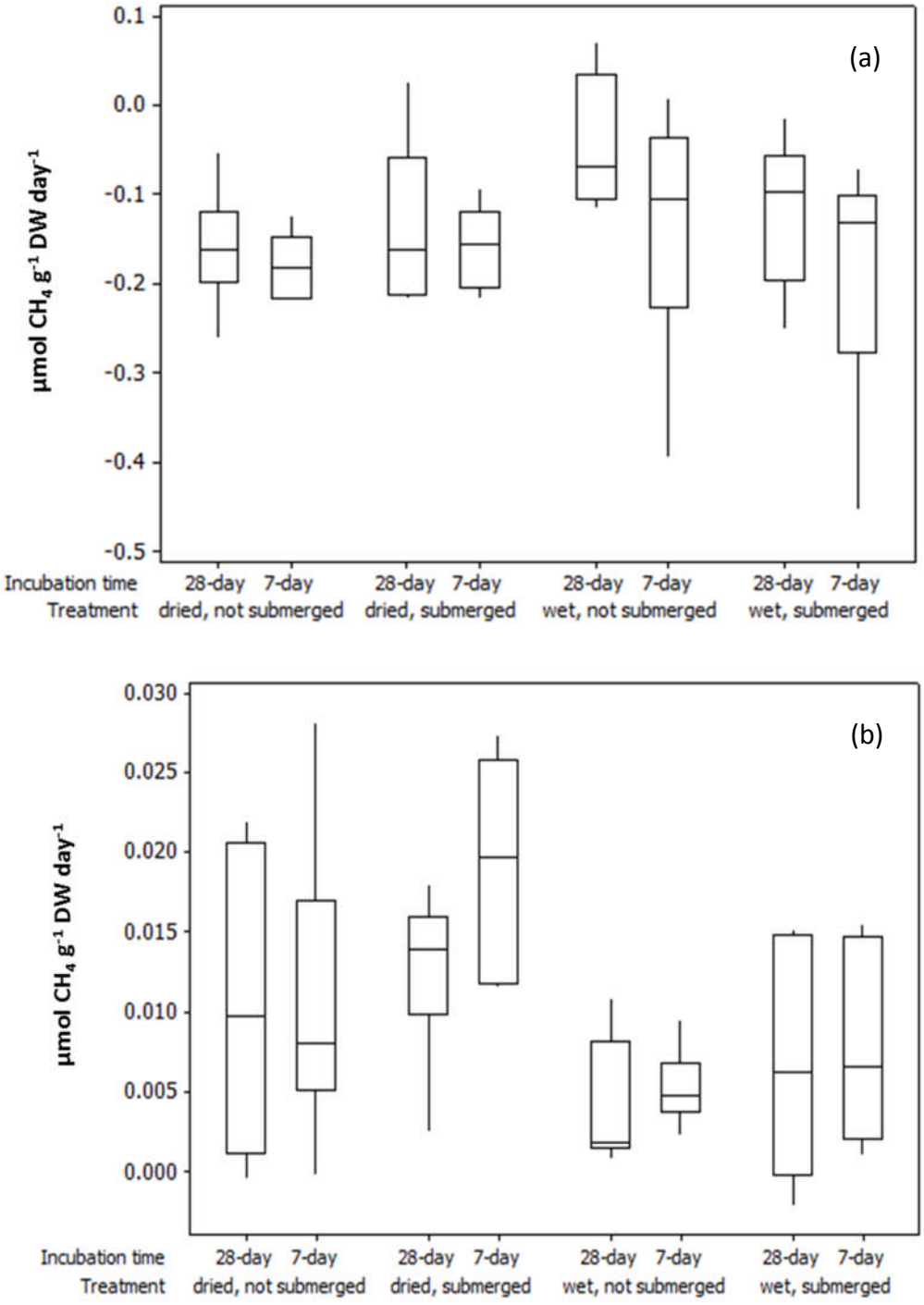

Figure 6.6: Boxplot of incubation and treatment results (a) with CH_4 added, (b) without CH_4 added. Negative values indicate methanotrophy, positive values indicate methanogenesis. Plotting convention as in Figure 4.2

Based on the literature, it was expected that the sub-samples in wet treatments would show higher rates of methanotrophy than in the dried treatments. Figure 6.6a shows the maximum rates for the two 7-day wet treatments were -0.39 µmol CH_4 g^{-1} day^{-1} (not submerged) and -0.45 µmol CH_4 g^{-1} day^{-1} (submerged). However, both of these wet treatments for the 7-day incubations also showed the lowest rates of methanotrophy at -0.076 µmol CH_4 g^{-1} day^{-1} (not submerged) and -0.07 µmol CH_4 g^{-1} day^{-1} (submerged). For the 28-day incubations, the sub-sample that produced the highest rate of methanotrophy was from the dried and not submerged treatment at -0.26 mg CH_4 m^{-2} day^{-1}. In the 28-day incubations there were also two sub-samples where the resulting fluxes were positive (CH_4 release from the *Sphagnum*), indicating that methanogenesis was occurring in these sub-samples. One sub-sample was in the dried and submerged treatment (0.026 µmol CH_4 g^{-1} day^{-1}), and the other from the wet and not submerged treatment (0.023 µmol CH_4 g^{-1} day^{-1}). There was only one sub-sample in the 7-day incubations that showed methanogenesis, from the wet and not submerged treatment (0.0075 µmol CH_4 g^{-1} day^{-1}).

6.3.4 Effects of PAR levels

Figure 6.7 shows that there was a significant relationship between rates of methanotrophy and levels of PAR in the wet and submerged treatment from both the 7-day (a) and 28-day (b) incubations. For all of the other treatments, there were no significant relationships between rates of methanotrophy and PAR. The relationship is slightly stronger and more significant for the 7-day incubation, based on the r^2 and *p*-values. The presence of this relationship in both incubation durations increases its validity. The direction of this relationship was unexpected based on the literature. As displayed in Figure 6.7, the rates of methanotrophy decrease with increasing PAR levels, which does not support the hypothesis of a 'symbiosis' between methanotrophs and *Sphagnum*, as suggested in the literature.

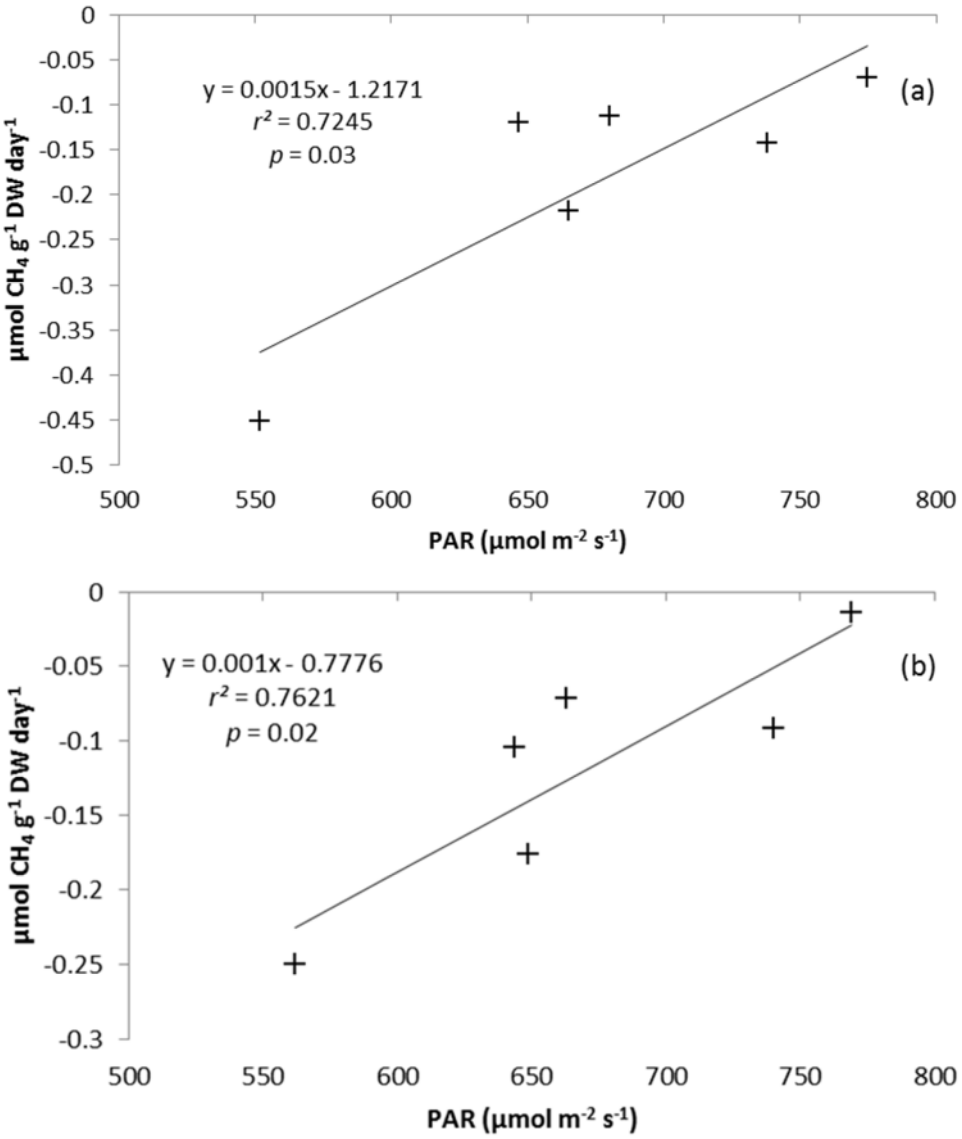

Figure 6.7: Relationship between PAR and methanotrophy for (a) 7-day, (b) 28-day wet and submerged treatment (low area, lower %).

6.4 Discussion

6.4.1 Effects of submergence on methanotrophy

The reported mutually-beneficial relationship between methanotrophs and *Sphagnum* mosses when the *Sphagnum* mosses are submerged (Raghoebarsing et al., 2005) was not found in the results of this experiment. If this relationship

between *Sphagnum* mosses and methanotrophs did exist, a significant difference would have been expected between the submerged and unsubmerged treatments. Figure 6.6a shows that the mean fluxes from each of the four treatments where CH_4 was added were all very similar, between -0.05 and -0.2 µmol CH_4 g^{-1} DW day^{-1}, and factorial ANOVA confirmed that there were no significant differences between any of the three factors (drought, submergence and incubation period). However, the sub-samples in the wet and submerged treatments were allowed to grow above the maintained water level within the incubations; therefore, this change in treatment conditions could be a reason for the wide range of values shown for these treatments in Figure 6.6. Larmola et al. (2010) showed that the most important control over methanotrophic activity in *Sphagnum* mosses was water content; a result that is not evident in this study. However, Basiliko et al. (2004) reported that *Sphagnum* species was a more important control than water content. If a different or multiple species of *Sphagnum* instead of just *S. cuspidatum* had been used in this study, then this theory could have been tested. As Figure 2.2 shows, it would have been expected to find a significant difference in methanogenesis between levels of submergence, because of the preference of methanogens for anoxia. However, it was only the submerged incubations where anoxic conditions were present; the sub-samples were removed from their submerged state for the chamber flux measurements, which may have affected results. Similarly, submerged conditions would have been expected to produce lower rates of methanotrophy (Figure 2.2), yet the sub-sample removal from anoxic conditions for the chamber flux measurements may have affected the results.

Figure 6.7 shows that the relationship between PAR and methanotrophy was not what would be expected for sub-samples that were wet and submerged if this mutually-beneficial relationship did exist. With increasing PAR levels, the rate of methanotrophy declined. Increased PAR would suggest an increase in photosynthesis, producing more O_2 and therefore allowing more methanotrophy. However, it is recognised that the sub-samples did not have a ready supply of CH_4 during incubation, as would have been the case in the field from the peat below.

Although more O_2 may have been available through increased photosynthesis, the concentrations of CH_4 available during incubation were similar to ambient concentrations at 2.1-2.3 ppm. Therefore, the methanotroph population within the *Sphagnum* mosses may not have grown during incubation, which may be a reason for the lack of any relationship observed. Also, during the flux measurements, the sub-samples were exposed to very low levels of PAR because they were no longer in the environmental cabinet. The reason for the decline of methanotrophic activity with increasing PAR could also be due to the growth displayed in the wet and submerged sub-samples, as shown in Figure 6.4d. If the *Sphagnum* mosses were growing during incubation, but the methanotroph population remained constant, then there would be fewer methanotrophs per gram of *Sphagnum*. However, efforts were made to counteract the potential effects of varying PAR levels through the randomised block design of the cabinet placement plan (Table 6.7). Each treatment had one sub-sample randomly placed within each of the six designated 'PAR blocks', and the average PAR level for each treatment was then as similar as possible (Table 6.6). Therefore, the relationships shown in Figure 6.7 could have occurred by chance. However, given that the same significant relationship was found for the same treatment for both incubation periods and not in any other treatments indicates that further study may be useful to better identify the effects of PAR on rates of methanotrophy within *Sphagnum* mosses.

6.4.2 Effects of drought on methanotrophy and methanogenesis

The lack of significant differences found between the wet and dried treatments shown in Figure 6.6a indicates that the drying of sub-samples had no effect on the ability of methanotrophs residing within *S. cuspidatum* plants to function. If drought did have an effect on methanotrophy it would have been expected to find fluxes from the dried treatments to be statistically different from the wet treatment fluxes.

Unfortunately no measures were taken to quantify if the seven days of drying that the sub-samples were subjected to prior to incubation damaged the photosynthetic abilities of the plants. From Figure 6.4a and Figure 6.4b it appears that the drying weakened the defences of the *Sphagnum* mosses to fight off algal and mould growths, and the plants are not as green as those in Figure 6.4c and Figure 6.4d, which suggests some effect on photosynthesis. However, the potential effects on photosynthetic abilities were not specifically measured.

If the pre-incubation drying did affect the methanotrophs living within the *Sphagnum* cells, the daily addition of field water to the sub-samples whilst in incubation may have negated these effects. Larmola et al. (2010) added filtered and non-filtered field water to *Sphagnum* samples that had been previously determined to have no methanotrophic activity. The non-filtered water caused the establishment of a methanotrophic community (Larmola et al., 2010). Putkinen et al. (2012) reported that methanotrophs can be transported through water; although Raghoebarsing et al. (2005) and Kip et al. (2010) indicated that methanotrophs do not function when present in water; only when they are residing within *Sphagnum* mosses. If drying was affecting the methanotrophic populations within the *Sphagnum* mosses and the field water was adding new methanotrophs to the sub-samples, it would have been expected to see more methanotrophy in the wet treatments in comparison to the dried treatments. If the methanotrophs in the dried treatments had declined, but those in the wet treatments had not, the populations within the wet treatments would be larger than those in the dried treatments through the daily addition of field water during incubation. However, although the wet treatments showed a wider range of methanotrophic activity, there were no statistically significant differences when compared against the dried treatments. The lack of statistical differences indicates that drying had no effect on the methanotrophs, and that active methanotrophs may not have been added to the sub-samples. An additional factor that should be taken into account when interpreting these results is that the containers in which the sub-samples were housed were washed with a decontaminating fluid, but were

not sterilised before use and between incubations. Therefore, it is not impossible that some microbial agents may have been present in the containers before use that could have influenced the 7-day incubations. Also possible, but perhaps unlikely, is that some microbial agents from the 7-day incubations could have survived within the containers and been passed on into the 28-day incubation sub-samples.

Interestingly, drought did have an effect on methanogenesis, with dried treatments producing significantly higher rates of methanogenesis than wet treatments. Due to the preference of methanogens for anoxic conditions, it would have been expected that wetter treatments would have higher rates of methanogenesis; however, the results showed the opposite trend.

6.4.3 Effects of temperature on methanotrophy

Dedysh and Panikov (1997) found that methanotrophic activity sharply declined with temperatures above 20 °C. Parmentier et al. (2011) and Kip et al. (2010) recorded increasing methanotrophic activity with increasing temperatures, although the maximum temperature in both studies was 20 °C. van Winden et al. (2012) reported results in agreement with Dedysh and Panikov (1997) in that the maximum methanotrophic potential was recorded at 20 °C, with a decline at 25 °C. The temperatures recorded during the chamber flux tests were mostly between 22-24 °C. These high temperatures during the chamber flux tests suggest that methanotrophy may have been suppressed, and so the rates of methanotrophic activity reported here could be underestimates.

6.4.4 Comparison with other studies

Overall, the rates of methanotrophy in *Sphagnum* mosses found in this study are much smaller than the rates found by other studies that also studied methanotrophy in *Sphagnum* mosses (Basiliko et al., 2004; Kip et al., 2010; Larmola et al., 2010; Parmentier et al., 2011; Putkinen et al., 2012; Raghoebarsing et al.,

2005; van Winden et al., 2012). The smallest range of methanotrophic activity from the *Sphagnum*-based studies in Table 6.2 was from Putkinen et al. (2012) at 0-18 µmol CH_4 g^{-1} DW day^{-1} in samples of *Sphagnum magellanicum* and *Sphagnum majus*. However, the maximum methanotrophic rate found in this study was much smaller at only 0.451 µmol CH_4 g^{-1} DW day^{-1} (Table 6.8). Although, Putkinen et al. (2012) determined detectable rates of methanotrophy as > 0.12 µmol CH_4 g^{-1} DW day^{-1}, which is higher than the rates detected in many of the sub-samples in this study. Putkinen et al. (2012) used gas chromatography to determine CH_4 concentrations, which shows that the methods used to determine methanotrophic activity can influence the results found.

All of the studies in Table 6.2 added much higher CH_4 concentrations to their sub-samples than in this study, which may be a reason for the higher rates of methanotrophy found in these other studies. However, Basiliko et al. (2004) added the smallest CH_4 concentration to the *Sphagnum* samples at 1000 ppmv and found the largest range of methanotrophic activity from slightly negative to 197 µmol CH_4 g^{-1} DW day^{-1}. There are reported to be two different types of methanotrophic activity; high affinity and low affinity. Le Mer and Roger (2001) suggested that high affinity methanotrophy occurs at CH_4 concentrations between 12 and 40 ppm; however, Segers (1998) sets the boundary much higher at CH_4 concentrations between 100 and 1000 ppm. At 1000 ppm, Basiliko et al. (2004) supplied *Sphagnum* samples with a CH_4 concentration that could have stimulated activity from both high and low affinity methanotrophs, which could explain the wide range of results found. Therefore, if the affinity boundary range suggested by Segers (1998) is accurate, the CH_4 concentrations supplied to the *Sphagnum* samples in this study would only have stimulated high-affinity methanotrophs; whereas all of the studies in Table 6.2 added CH_4 concentration that only low-affinity methanotrophs could consume, which could explain the difference in results between this study and those in Table 6.2.

The results of this study of *Sphagnum* mosses also show much smaller methanotrophic rates than most other studies in Table 6.2 where methanotrophy in peat was the focus (McDonald et al., 1996; Rinnan et al., 2003; Sundh et al., 1995). Moore and Dalva (1997) reported a mean methanotrophic rate of 0.82 µmol CH_4 g^{-1} DW day^{-1}, which is much closer to the maximum rate found in this study (0.451 µmol CH_4 g^{-1} day^{-1}). The minimum rate of methanotrophy found in peat slurries by Bellisario et al. (1999) was 0.25 µmol CH_4 g^{-1} DW day^{-1}, which is similar to the maximum rate found in the 28-day incubation sub-samples of this study (0.261 µmol CH_4 g^{-1} DW day^{-1}).

Several studies shown in Table 6.2 examined methanotrophic activity in different parts of the *Sphagnum* mosses. Basiliko et al. (2004) split the plants into top, middle and bottom sections depending on their colour (green, white and brown). van Winden et al. (2012) split the plants in top, middle and bottom parts using a different method; each part was a 3 cm segment. Both studies found that although the bottom parts of the plants had the higher values of methanotrophy, there was no statistically significant difference between the three separate parts (Basiliko et al., 2004; van Winden et al., 2012). Raghoebarsing et al. (2005) separated *Sphagnum* mosses into three 10 cm segments; however, no statistical tests for differences in methanotrophic activity between the three parts were reported.

In one of the 7-day sub-samples to which CH_4 was added and three of the 28-day sub-samples to which CH_4 was added, there was evidence of methanogenesis occurring, despite the addition of CH_4. Only one other study (Basiliko et al., 2004) reported evidence of methanogenesis, although an exact value was not presented. Kip et al. (2010), Larmola et al. (2010) and Putkinen et al. (2012) all reported the lowest rate of methanotrophy found as zero, but it is unclear as to whether methanogenesis was not detected or just excluded from the results. Larmola et al. (2010) examined 23 species of *Sphagnum*, including *S. cuspidatum*, and found that not all samples analysed showed methanotrophy. Of the 23 species, only the

samples from nine species found in the wettest environments showed methanotrophy in every sample, whereas for *S. cuspidatum* only 60 % of the samples showed methanotrophy (Larmola et al., 2010). In this study, of the 48 sub-samples where CH_4 was added, 91.7 % showed methanotrophy.

There were also three sub-samples where CH_4 was not added that showed methanotrophic activity. Interestingly, two of these sub-samples were from treatment 7, replicate 3 (dried and not submerged), with the third from the 28-day wet and submerged treatment (0.0021 µmol CH_4 g^{-1} DW day^{-1}). In both the 7-day and 28-day incubations, sub-sample 7_3 showed very small rates of methanotrophic activity (0.0002 and 0.0005 µmol CH_4 g^{-1} DW day^{-1} respectively). Given that these two sub-samples were separate plants and were incubated for different lengths of time, the only common factor between the two sub-samples was the cabinet placement position, which suggests that PAR levels may be the influential factor. However, given that this sub-sample was the third replicate of the treatment, it was located within the third PAR 'block' of the randomised block design. Therefore, if PAR did have an influence, it would be expected to see increasing or decreasing rates of methanotrophy in replicates 1 and 2 or 4-6. These patterns were not observed, nor was there any statistically significant relationship between PAR and rates of methanotrophy for this treatment, which suggests that this particular result may just have been a chance similarity.

6.5 Conclusions

Overall, for research questions 5 and 6, this experiment showed a lack of any effects of drought or submergence on the abilities of methanotrophs to oxidise CH_4, and a lack of evidence for a mutually-beneficial relationship between methanotrophs and *S. cuspidatum*. Where land managers are restoring peatlands and *S. cuspidatum* is present, a period of drought may not cause inhibited methanotrophic activity and therefore larger CH_4 fluxes to the atmosphere.

However, increased methanogenesis in *S. cuspidatum* plants that have experienced drought may negate the lack of reduced methanotrophy. *Sphagnum cuspidatum* is a common species found on restored peatlands; however, Larmola et al. (2010) found that certain species of *Sphagnum* showed a higher proportion of methanotrophic activity than others. Of the 23 species studied, 18 species displayed more methanotrophic activity than *S. cuspidatum* (Larmola et al., 2010), which suggests that if land managers could encourage other species of *Sphagnum* to grow, then CH_4 emissions could be reduced. Although, it is unknown if the low methanotrophic rates reported in this study are purely a result of the *Sphagnum* species, or whether there are other factors in play. Thorne Moors could potentially receive a lot of atmospheric deposition from air pollution due to its location between three power stations, and its proximity to an airport, and it is unknown if these potential factors may influence methanotrophy. The conditions witnessed during fieldwork at Hatfield Moor, where the *S. cuspidatum* was sometimes dry and constantly not submerged may not have been preventing methanotrophic activity as originally thought. These results suggest that the CH_4 fluxes presented for Site D in Chapter 4 are not over- or underestimations in terms of the effects of methanotrophic activity.

However, it is recognised that this experiment could have benefited from certain improvements. Overall, the results of this experiment have proved to be more observational rather than a scientific test of a hypothesis. All of the sub-samples that were not submerged still had access to water via the bottom of the plants. A treatment where plants had no access to water would have provided further insight into the effects of both drying and submerging sub-samples. The addition of field water to the sub-samples during incubation may have released additional methanotrophs, despite the lack of evidence in the results to support this theory. The effects of drying on the photosynthetic abilities of the sub-samples were unquantified, as were the amount of methanotrophs present within the *Sphagnum* cells before and after incubations and chamber tests. Knowledge of both of these factors may have enabled a stronger interpretation of the results of this

experiment. Microscopic analysis of the hyaline cells of the *Sphagnum* mosses before and after drying may have provided information as to whether drying did affect these cells in any way, which may have had a knock-on effect to the preference of methanotrophs for residing there. Only one cycle of drying was used in this experiment; an experiment using various cycles of drying and rewetting would help to understand if repeated drying had a greater effect on methanotrophy than just one period of drought. Also, the effects of the length of the period of drought was not examined in this experiment; a factor that may also have an impact on methanotrophic activity.

If this work were to be repeated, a third treatment where the sub-samples had no access to water would allow for a further test of the effects of water. Many other authors (as detailed in Table 6.2) used deionised water in their experiments, without a clear rationale for that choice. Given the possibility that the use of field water in this experiment may have influenced the results, a repeat of this study using only deionised water would remove the uncertainty that additional methanotrophs may have been added to the sub-samples. Intensive field monitoring at Site D, where the *S. cuspidatum* was experiencing a fluctuating WTP could have provided further insight into the research questions posed for this section of the thesis. Although the collars for the work presented in Chapter 4 were located in an area of Hatfield Moors (Site D) where the WTP did not return to the near-surface following a dry summer, there were other areas also dominated by *S. cuspidatum* where the WTP did recover during the course of the study period. Additional flux chamber tests in areas with a higher WTP than Site D could have provided a useful comparison on the effects of the WTP on CH_4 fluxes. However, because the WTP can also affect methanogenesis as well as methanotrophy, a laboratory study is likely to provide better results.

Chapter 7: Conclusions

7.1 Conclusions

7.1.1 Overall findings and contributions

This study explored the effects of peatland restoration on fluxes of CH_4 and CO_2 at Thorne and Hatfield Moors and also considered the effects of diurnal changes in emissions, as well as how drought and submergence could affect the abilities of methanotrophs living in *S. cuspidatum* plants to function. Six research questions were addressed:

1. **Do CH_4 and CO_2 emissions from peatlands change with time following restoration?**
2. **What are the main drivers of CH_4 and CO_2 emissions in restored peatlands?**
3. **Do CH_4 emissions vary diurnally, and if so, what are the main drivers of the diurnal variations?**
4. **Does the diurnal variation in CO_2 emissions result in positive or negative NEE?**
5. **Does drought affect methanotrophic activity within *Sphagnum* mosses?**
6. **Does submergence affect methanotrophic activity within *Sphagnum* mosses that have been subjected to drought?**

Research question 1 could not be answered in full due to a lack of successful models of P_G and R_{TOT} for each of the 24 collars, which meant that NEE and subsequent GWP values were not calculated for every collar. However, the partial findings from the six collars where NEE and GWP could be calculated indicated that there were no obvious benefits from restoration. In terms of NEE, all six collars were net emitters of CO_2 and overall, there were greater CO_2 emissions from the collars at Sites A and B (restored in 1997 and 2003 respectively) than from Site C

(control). From the conceptual diagrams in Figure 2.1, it was expected that the CO_2 emissions from Site C would be greater than from Sites A and B due to the differences in WTP, and therefore the extent of the oxic and anoxic zones. Many other studies, as detailed in Sections 2.2.2.4 and 2.2.3 have found vegetated peatland areas to have negative NEE values; a pattern that was not replicated at Thorne and Hatfield Moors with the limited data available. Methane emissions were significantly higher at the two older sites (A and B) than at the control site (C). Therefore, overall, the GWP values were all positive (net warming effect) and were higher from Sites A and B than from Site C. These findings, although from a small dataset, contradict the hypotheses of Joosten et al. (2006) and Bain et al. (2011) which both predicted a decrease in GWP with time since restoration, as shown in Figures 2.2 and 2.3. Joosten et al. (2006) proposed three different timescales for their hypothesis; only the first of which could be tested in this study. The best-case timescale indicated that after five years, the GWP would start to decline (Joosten et al., 2006). Bain et al. (2011) predicted that GWP values would show decline within the first ten years post-restoration, but Site B has been restored for more than five years and Site A for more than ten years and the GWP data from the four collars at those sites show no evidence of a GWP decline. Due to the lack of NEE and GWP data from Site D - the most recently restored site (2008) - it was not possible to conclude if either of the hypotheses on long-term responses of gaseous fluxes to peatland restoration developed by Bain et al. (2011) or Joosten et al. (2006) were accurate in terms of the initial responses of gaseous fluxes to restoration. Joosten et al. (2006) predicted an initial spike in GWP in the first years following restoration; a rise above levels when the peatland was drained. However, Bain et al. (2011) predicted that in the first ten years of restoration starting, the GWP of a peatland will decrease from pre-restoration levels, but there will still be a net loss of carbon to the atmosphere. Given the lack of GWP data for Site D, this research is unable to contribute any evidence towards either hypothesis for the initial few post-restoration years. Due to the data from the ebullition funnels deployed at Sites A and B being of insufficient quality to be used in this thesis, the overall fluxes from these sites may be underestimates.

To address research question 2, drivers of CO_2 fluxes were assessed using the P_G and R_{TOT} model results, but due to the lack of acceptable models, this analysis was limited. Soil temperature was the main driver of R_{TOT}, and solar radiation combined with either WTP and air temperature, or soil temperature and ETI (a variable to take into account the effects of the growing season) (Tuittila et al., 1999) were the main drivers of P_G. However, these models were constructed using a limited range of environmental variables, as defined by Tuittila et al. (1999) or Samaritani et al. (2011). Drivers of CH_4 fluxes were analysed on a per-site basis using multiple linear regression. The results showed that on Sites A, B and D there was one collar on each site that had a disproportionate effect on the model. For Site A it was the collar where there was some bare peat cover during the winter months which coincided with zero CH_4 fluxes. For Site B it was the collar where there was some *Sphagnum cuspidatum* cover during the summer months when the onset of the growing season caused a rise in the CH_4 fluxes. For Site D it was the one collar that contained a small tussock of *Eriophorum vaginatum*, which produced increasingly larger fluxes as the growing season progressed, unlike the other Site D collars where the CH_4 fluxes showed little response to the growing season. Average air temperature over either the past 72 or 168 hours was included in the models for Sites A, B and C, and WTP featured in the models for Sites A and B. Cumulative solar radiation was included in the models for Sites B and C. Peat depth was in the models for Sites A and C, but there were no other similarities between the results. No variable was included in all the models from the sites, suggesting that there are different drivers on different sites.

The results from the diurnal study (Chapter 5) suggest that the fluxes reported in Chapter 4 are likely to be underestimations. The work to address research question 3 found that CH_4 emissions were significantly greater at night, with air temperature as a main driver for two of the four collars studied. All CH_4 fluxes reported in Chapter 4 were measured during the daytime. The work to address research question 4 found that each collar had a net loss of CO_2 to the atmosphere. Collars A5 and A6 were included in both the diurnal study, and had accepted P_G and

R_{TOT} models, from which NEE could be calculated. For collar A5, the diurnal results (11.8 g CO_2 m^{-2} day^{-1}) and NEE results (4594 g CO_2 m^{-2} day^{-1}) were in agreement over the same 24-hour period, in that both sets of results showed a net loss of CO_2 to the atmosphere. However, there is a large difference between the measured and modelled results, which may be due in part to a fault with the AWS, where solar radiation could not be logged, and so there are missing hours of P_G results in the NEE results for this 24-hour period. For collar A6, the diurnal results (10.1 g CO_2 m^{-2} day^{-1}) and the NEE results (-1354 g CO_2 m^{-2} day^{-1}) were not in agreement for the same 24-hour period. As well as the same AWS fault influencing the P_G model, the R_{TOT} model for collar A6 had a comparatively low (0.42) r^2 value, which could also have influenced results. Carbon dioxide fluxes measured at night-time were larger than any CO_2 fluxes measured using dark chambers, indicating that the dark chamber method does not accurately imitate night-time conditions, other than blocking the light. Therefore, the results of the R_{TOT} models presented in Table 4.4 may be underestimations. Underestimations of R_{TOT} and night-time CH_4 fluxes would mean that the NEE and GWP totals presented in Table 4.5 are also underestimates. Site B had similar vegetation cover and WTP to Site A, and so are likely to have had a similar diurnal response. The absence of vascular plants at Sites C and D would probably result in different diurnal responses of CH_4 and CO_2 fluxes.

From the results presented in Chapter 6, there was no evidence that drought or submergence of *Sphagnum cuspidatum* plants affects the ability of methanotrophs, (research questions 5 and 6). Neither was there any evidence of any mutually-beneficial relationship between *S. cuspidatum* and methanotrophs Therefore, although the WTP at Site D was much lower than expected throughout the entirety of the data collection period for this study, these results suggest that these conditions were not hindering methanotrophic activity in the top part of the peat profile occupied by *S. cuspidatum*. Drought did affect rates of methanogenesis in the control treatments, with *S. cuspidatum* that were dried out prior to incubation showing higher rates of methanogenesis than those plants that remained wet.

There were several aspects of this research which suggest that the NEE and GWP values reported in Chapter 4 may be underestimations. Episodic ebullition fluxes were not included, and the results of the diurnal study showed that CH_4 fluxes were significantly larger during the night, and that the method for measuring ecosystem respiration using static closed chambers during the daytime did not accurately replicate night-time conditions.

Overall, this work has contributed another dataset to the small number of existing datasets on peatland gaseous fluxes where restoration has been on-going for an excess of ten years. It has shown, in part, that the theories depicted in Figure 2.1 and the hypotheses presented in Figures 2.2 and 2.3 do not hold true for this particular peatland. Peatland restoration at Thorne and Hatfield Moors does not appear to be having the desired effect in terms of gaseous fluxes of CH_4 and CO_2, and the resulting GWP values. Sites where restoration began either nine or 15 years prior to this research showed similar (if not higher) rates of NEE to the control site where restoration has not yet occurred (although the small size of the dataset is acknowledged). Methane fluxes were significantly larger at the two older sites in comparison with the control site, and the site where restoration began four years prior to this study. Therefore, the hypotheses presented by Joosten et al. 2006 and Bain et al. 2011 may need to be revised, should further evidence to support the traits shown in this study emerge. Both hypotheses indicated that the GWP values of restored peatlands should start to decline as soon as five or ten years after restoration started; yet, the two oldest sites studied at Thorne Moors had restoration start dates more than five and ten years prior to this study, and have shown no signs of the gaseous fluxes and resulting GWP values conforming to these hypotheses.

Studies where CH_4 flux measurements only occur during the daytime could be reporting underestimated fluxes, because this study showed, from one set of

observations, that CH_4 emissions were significantly greater at night-time from areas dominated by *Eriophorum* spp. Chamber flux measurements of CO_2, where R_{TOT} is measured using a shrouded chamber are also likely to be underestimations, because the results of this study showed that fluxes measured during one night were larger than any dark chamber fluxes reported throughout the entire year at the same site.

7.1.2 Implications for peatland management

The CH_4 fluxes from Sites A and B were significantly larger than those from Sites C and D. The two main differences between these two sets of sites were WTP and vascular plant cover. However, it is unclear as to which (if either) of these two variables may be responsible for the differences. The models to identify CH_4 flux drivers per site identified WTP as a driver for both Sites A and B, but vegetation cover variables (*E. vaginatum* and *S. cuspidatum*) were only included in the model for Site B. The vascular plant cover at Sites A and B is likely to be a result of successional changes within the vegetation cover. However, these plants allow for increased CH_4 emissions to the atmosphere by providing a transport pathway out of the deeper anoxic layers where methanogenesis occurs, and also provide substrates for methanogens through root exudation, increasing CH_4 production. As the CO_2 modelling results show, these areas dominated by vascular plants can produce a wide range of NEE values. All four of the NEE values for Sites A and B were positive, and therefore did not counterbalance the high CH_4 fluxes. However, it is recognised that CH_4 flux totals were calculated for all six collars on both sites, whereas NEE values were only calculated for four out of these twelve collars. It is unknown whether the remaining eight collars would also have resulted in positive NEE values. It may be that the root exudates from the *Eriophorum* cover at Sites A and B were not only stimulating methanogenic activity, but were also allowing for the decomposition of 'old' carbon stored within the peat. There were lower CH_4 fluxes from Sites C and D than from A and B, which from a land management perspective in terms of carbon storage could be interpreted as bare peat or a

Sphagnum cover with a low WTP is better than a high WTP with vascular plant cover. However, from a biodiversity perspective this option would be far from ideal. The two collars at Site C for which NEE could be calculated still had a net CO_2 loss and therefore a positive GWP value. Both of these GWP values were higher than for one of the collars at Site A. If the other collars at Site C and those at Site D respond in the same way as these two collars at Site C, then the conditions at these two site could still not be classed as in ideal conditions to produce a negative GWP (net cooling).

In summary, the key messages are:

- CH_4 fluxes were significantly greater from areas dominated by *Eriophorum* spp. with a high WTP (at peat surface or surface inundation) than from areas with a low WTP dominated by *Sphagnum cuspidatum*. or without vegetation cover.
- There was little difference between the NEE of the restored and unrestored sites (although the dataset was very small), and of the six collars for which this modelling was possible, all showed a net loss of CO_2 to the atmosphere.
- R_{TOT} values were larger at the sites dominated by *Eriophorum* spp. with a high WTP than from the control site with a low WTP and no vegetation cover.

7.2 Further work

The monitoring of gaseous fluxes for this study lasted 13 months, which provided enough data for annual CH_4 fluxes for every collar to be calculated and compared. However, monitoring for one year does not allow for any possible inter-annual variability to be observed. For example, the three years prior to this study all had below-average rainfall, yet 2012, the year in which the majority of the data collection occurred, had above-average rainfall and was the wettest year between

1992 and 2012. Without any other annual data from Thorne and Hatfield Moors to compare the results of this study to, it is unclear what effect the increased rainfall, and subsequent higher WTP may have had on the gaseous fluxes in comparison to drier years. A larger dataset may also have resulted in more accepted CO_2 models, which would have provided further insight into the NEE and GWP values on a per-site basis, rather than the current per-collar basis. Information of the NEE and GWP values on a per-site basis would then have allowed for comparisons and conclusions to be made with regards to the effects of time since restoration started. Significant differences were found between sites for CH_4 fluxes, where an annual flux was calculated for every collar; the ability to do the same for NEE and consequently GWP would be highly beneficial. On each site, the collars were placed to encompass the dominant vegetation type of the restoration compartment; although other vegetation types were present at each site. It would be interesting to know what the gaseous flux trends from these other vegetation types are to see if they contribute to or abate the trends found in this study. In general, any further work on peatlands where restoration started more than ten years ago would help to fill the current gap in the literature and would aid the development of long-term peatland management where gaseous fluxes of CH_4 and CO_2 are of interest.

An extension of the research presented in Chapter 5 on the diurnal responses of gaseous fluxes would be beneficial. Fluxes were measured over one diurnal cycle, and it was only possible to measure from four collars. Wider replication, both of collar numbers and diurnal cycles would provide further evidence of the drivers of CH_4 flux, which in this research could not be identified for all four collars. Within the literature reviewed for this area of research, as shown in Table 5.1, there was very little replication of studies on peatlands with similar vegetation cover. It is recognised that many peatlands support a diverse range of plant species. However, a lack of replication in this wider sense means that it is still unknown

whether fluxes from areas with similar vegetation cover will respond to diurnal changes in controlling environmental variables in the same way on different peatlands.

The *Sphagnum* mesocosm experiment would have benefited from several improvements. An extra treatment where *Sphagnum* samples had no access to water at all would have provided further insight into the effects of drought. An additional experiment whereby the same samples were subjected to drought, re-wetted and tested, then subjected to drought again may have better simulated the conditions observed at Site D.

Overall, this research has made significant findings that have implications for future work in this area. Peatland restoration has not had the expected effect on gaseous fluxes at Thorne and Hatfield Moors; restoration had not resulted in a lower GWP. With increasing time since restoration started, CH_4 fluxes were significantly larger at the two older restored sites than the younger restored site and the control site. Also, R_{TOT} was larger at the two older restored sites in comparison to the control site (although the small size of this particular dataset is acknowledged). Restoration is generally defined by the WTP and vegetation cover on a peatland. Given the results of this study, efforts by peatland managers to constantly keep the WTP near the peat surface does not appear to be as beneficial for gaseous flux management as previously thought. Although, the control site has been in its current state since 2003. If measurements had occurred shortly after milling had ceased, the results of this study could have been different. It might be that by 2012 only the recalcitrant carbon was left within the peat at Site C, which could be the reason for the lower NEE and CH_4 fluxes at this site, rather than the WTP. Allowing a vascular plant cover to establish could have carbon sequestration benefits whilst the plants are growing, but the data from Sites A and B suggest that when the plants are no longer young, they contribute to a positive GWP balance.

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