



# THE UNIVERSITY *of* EDINBURGH

This thesis has been submitted in fulfilment of the requirements for a postgraduate degree (e.g. PhD, MPhil, DClinPsychol) at the University of Edinburgh. Please note the following terms and conditions of use:

This work is protected by copyright and other intellectual property rights, which are retained by the thesis author, unless otherwise stated.

A copy can be downloaded for personal non-commercial research or study, without prior permission or charge.

This thesis cannot be reproduced or quoted extensively from without first obtaining permission in writing from the author.

The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the author.

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given.

**Effects of drain blocking and nitrogen  
deposition on greenhouse gas emissions  
from peatlands**

Magnus P. C. Kelly

Doctor of Philosophy

The University of Edinburgh

2012

## **Declaration**

I declare that this thesis has been composed by myself and no part of it has been submitted for any other degree or professional qualification. The work included is my own unless stated.

Magnus Kelly

September 2012

## Abstract

Peatlands cover between 10 – 15 % of the UK landmass, yet contain 50 % of the UK soil carbon store. This is more than any other ecosystem and makes them the most important carbon store in the UK. Peatlands have been impacted by human activities such as drainage, grazing, burning and atmospheric pollution. Some of these activities are believed to have altered the carbon balance of peatlands, potentially causing them to release the carbon they store, exacerbating global warming. The current state of peatlands in the UK is not fully known and the extent to which carbon exchange is impacted by human impacts is not understood. This study uses field measurements and manipulative experiments to investigate the impact of human activities on carbon exchange.

CO<sub>2</sub> flux measurements were made at an experimental nitrogen addition field site to investigate the impact of atmospheric pollution. The addition of nitrogen was found to have no significant impact on net ecosystem exchange (NEE), ecosystem respiration (ER), or the vegetation community structure at any concentration of nitrogen deposition. A method was determined for estimating the vegetation biomass and subsequently the LAI and NEE based on a non destructive vegetation survey.

Peatland drainage was a widespread management practice across peatlands over the past century, however due to concerns about the practice many drains are currently being blocked. Measurements of water table, CO<sub>2</sub> and methane fluxes were made at a drained site before and after it was blocked. The drains were found to have a very limited impact upon water table, only reducing the water table by 6.7 cm within 50 cm of the drain and having no significant effect on gas fluxes. The blocking of drains raised the water table within 50 cm of the grip, however did not have any detectable impact on gas fluxes or vegetation.

The carbon balance of a pristine ombrotrophic was measured using continuous measurement methods and modelled fluxes to establish whether it was a sink or source of carbon. The site was found to be a sink of 155.5 g m<sup>-2</sup> y<sup>-1</sup> for CO<sub>2</sub> and source of 4.1 g m<sup>-2</sup> y<sup>-1</sup> CH<sub>4</sub>. The site was found to be a sink of 49.3 g m<sup>-2</sup> y<sup>-1</sup> for carbon once CO<sub>2</sub> and CH<sub>4</sub> were taken into account.

## **Acknowledgements**

I would like to thank my supervisors for the advice and support they have provided me with during the course of this work. I would also like to thank the facilities staff at the Centre for Ecology and Hydrology (Edinburgh) for providing and maintaining the facilities to make this possible.

I would like to thank the RSPB staff at Forsinard for permitting us to use the site for research and for offering help and assistance where needed. In particular advanced warnings of impassable roads due to flooding and heavy snow, to avoid long wasted journeys.

Many thanks go to the North Pennines Area of Outstanding Beauty Peatscapes project for their help in arranging for me to work at a site there and liaising with stakeholders for me. Particular thanks must go to James Scott-Harden and the Newbiggin Estate staff for allowing me to use the site for experiments and providing assistance while at the site.

Finally, I must thank my fellow students, friends and family for helping me to keep going to the end.

This project was a NERC algorithm funded studentship.

# Table of Contents

## CHAPTER 1 – INTRODUCTION AND AIMS

1.1	Introduction	8
1.2	Aims	20
1.3	Overview of thesis	21

## CHAPTER 2 - METHODS AND MATERIALS

2.1	Methods	23
2.2	Water table measurements	23
2.3	Flux chamber base	25
2.4	CO <sub>2</sub> flux measurements	28
2.5	Methane flux measurements	31

## CHAPTER 3 - THE IMPACT OF NITROGEN DEPOSITION ON CO<sub>2</sub> FLUXES FOR AN OMBROTROPHIC BOG

3.1	Introduction	38
3.2	Aims	42
3.3	Methods	43
3.3.1	Site description	43
3.3.2	Carbon dioxide measurements	47
3.3.3	Vegetation survey and harvesting	49
3.3.4	Data analysis and statistics	50
3.4	Results	51
3.4.1	NEE measurements	51
3.4.2	CO <sub>2</sub> Respiration	54
3.4.3	Vegetation survey and harvesting	57
3.4.4	Estimating biomass using the vegetation survey	58
3.4.5	Determining LAI from mass	64
3.5	Discussion	68
3.6	Conclusions	74

## CHAPTER 4 - THE IMPACT OF BLOCKING MOORLAND OPEN DRAINS ON THE PEATLAND CARBON BALANCE

4.1	Introduction	76
4.2	Aims	83
4.3	Methods	84
4.3.1	Field site	84
4.3.2	Water table measurements	86

4.3.3	CO <sub>2</sub> and Methane measurements	87
4.3.4	Data analysis and statistics	89
4.4	Results	90
4.4.1	Water table	90
4.4.2	NEE flux measurements	93
4.4.3	Ecosystem respiration measurements	97
4.4.4	Methane measurements	101
4.4.5	Vegetation biomass and LAI estimation	104
4.5	Discussion	109
4.6	Conclusions	114

## CHAPTER 5 - THE CARBON BALANCE OF AN UNDISTURBED OMBROTROPHIC PEATLAND

5.1	Introduction	116
5.2	Aims	121
5.3	Methods	122
5.3.1	Field site	122
5.3.2	Methane fluxes	123
5.3.3	CO <sub>2</sub> fluxes	124
5.4	Results	129
5.4.1	Environmental conditions	129
5.4.2	Methane fluxes	130
5.4.3	NEE measurements	138
5.4.4	Carbon balance	143
5.4.5	Global warming potential	145
5.5	Discussion	149
5.6	Conclusions	155

## CHAPTER 6 - SUMMARY, REFERENCES AND APPENDIX

6.1	Summary	157
6.2	References	161
6.3	Appendix A	187
6.3.1	Tables associated with Chapter 3	187
6.3.2	Tables associated with Chapter 4	191
6.3.3	Tables associated with Chapter 3	197

## **CHAPTER 1**

### **INTRODUCTION AND AIMS**

## 1.1 Introduction

Peatland ecosystems are characterised by high water tables resulting in anaerobic soil conditions and specialised vegetation. The anaerobic conditions caused by long periods of waterlogged ground inhibit the decay of dead plant material, resulting in the net primary production (NPP) from vegetation exceeding the decomposition of organic matter (Rydin & Jeglum 2006). The change in the amount of carbon stored within the ecosystem can be determined by the following equation:

$$\Delta C = - (NEE + F_{CH_4} + F_{DOC} + F_{DIC} + F_{POC}) \quad (1.1)$$

Where  $\Delta C$  is the change in carbon within the ecosystem, NEE is the net ecosystem exchange of  $CO_2$ , including NPP and Ecosystem Respiration (ER),  $F_{CH_4}$  is the flux of methane ( $CH_4$ ),  $F_{DOC}$  is the flux of dissolved organic carbon (DOC),  $F_{DIC}$  is the flux of dissolved inorganic carbon (DIC) and  $F_{POC}$  is the flux of particulate organic carbon (POC) within fluvial export (Marsden & Ebmeier 2012). In the components of equation 1.1 negative fluxes indicate a movement of carbon from the atmosphere to the ground, whereas positive fluxes indicate the movement of carbon from the ground to the atmosphere.

Where  $\Delta C$  is positive this leads to an accumulation of layers of organic matter in various stages of decomposition, forming the peat layer. Soil is considered to qualify as peat when the proportion of dead organic material exceeds 30 % of the dry mass. The term peatland refers to an area covered by peat soil, the depth of which should typically exceed 30 cm to be considered a peatland (Joosten & Clarke 2002).

Peatlands are found throughout tropical and boreal regions and globally cover around 3 % of land surface as seen in Fig.1.1. (Charman 2002). Soils are important reservoirs within the carbon cycle as it is estimated that they contain 1,500 Gt of carbon, roughly equivalent to the amount stored in the atmosphere and vegetation combined (Powlson 2005). In spite of the relatively small global cover, estimates of the amount of carbon contained in boreal peatland ecosystems range from 41.5 – 489 Gt (Buringh 1984, Armentano & Menges 1986, Gorham 1991, Turunen *et al.* 2002,

Wieder & Vitt 2006, GEC & WI 2008). This makes peatlands very important reservoirs within the carbon cycle as they potentially make up a third of the global soil carbon store in spite of only covering 3 % of the global surface area. The estimates of carbon stores indicate that peatlands globally store the equivalent of 75 % of the carbon currently in the atmosphere (Parish 2008). It has been calculated that the amount of carbon stored in peatlands over the past 10,000 years has reduced the global temperature by 1.5 – 2 °C (Holden 2005).

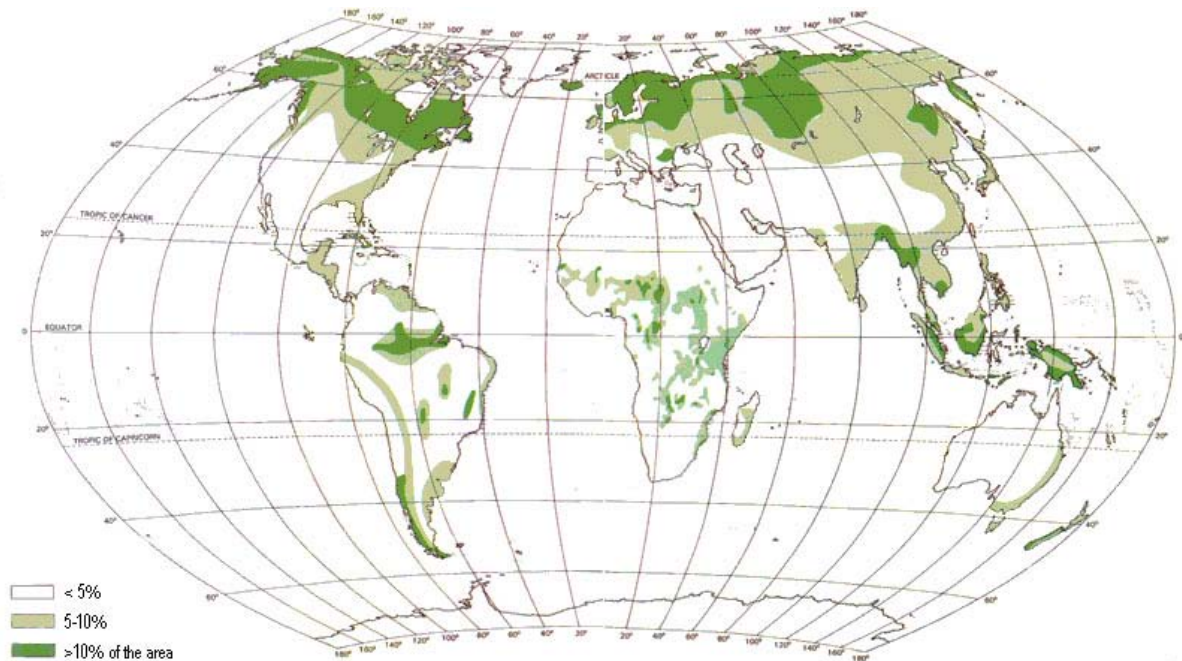


Figure 1.1. The global extent of peatlands in boreal and tropical areas. Source: EU LIFE project.

It has been estimated that 0.7 % of global peatlands are located in the UK (Clymo, 1984), covering 10.9 % of the UK land surface (Montanarella *et al.* 2006). For the UK, peatlands are more significant than they are globally as they store more carbon than any other UK ecosystem and contain 50.8 % of the soil carbon store (Milne & Brown 1997).

As well as being important stores of carbon, within the UK and internationally, peatlands are recognised as important ecosystems and habitats that need protection. Annex 1 of the EU Habitats and Species Directive (92/43/EEC) includes both raised bogs and blanket bogs, requiring members of the EU to protect and restore them to a

favourable conservation state. Peatlands are also protected habitats in the Ramsar convention, are often designated as Special Areas of Conservation and are listed as priority habitats under the UK Biodiversity Action Plan. One reason peatlands are considered important ecosystems within the UK is their rich biodiversity and the number of species that are dependent on them for their habitat, including species of butterflies, dragonflies, invertebrates, amphibians and birds of prey (Brooks 1997, Stoneman 1997, Stroud *et al.* 1988, Thompson *et al.* 1995). Peatlands are also home to a number of vegetation species that are specialised to living in the waterlogged, acidic and nutrient limited systems found there, including *Sphagnum* spp, *Calluna vulgaris* and species of *Erica* and *Vaccinium* (Rydin & Jeglum 2006, Thormann 2006).

Peatlands also provide a number of ecosystem services when in a functioning state. Up to 90 – 98 % of peat mass can be water (Holden 2005) and due to this ability of peat to absorb water, during periods of heavy precipitation they can regulate the amount of runoff, limiting flooding and act as filtration systems for water outflow (Keddy *et al.* 2009). Additionally, in the UK peatlands are often located in the remotest parts of the country due to their location in upland and extreme northern areas, which also makes them important as areas for people to use for recreational activities due to their large undeveloped areas.

During the 20<sup>th</sup> Century the global surface temperature was calculated to have increased by  $0.74 \pm 0.18$  °C (IPCC 2007). The upward trend can be seen in Fig. 1.2. and in particular the rapid rate of change from the 1970s onwards. This increase in temperature has already been linked with changes in species distribution, shrinking of glaciers and sea level rise (Diolaiuti & Smiraglia 2010, Thuiller *et al.* 2008, Meehl *et al.* 2012). As peatlands are typically slow changing systems due to lower rates of biological activity than other ecosystems, any rapid environmental changes leave them particularly vulnerable if they are unable to adapt quickly enough (Rydin & Jeglum 2006, Davidson & Janssens 2006).

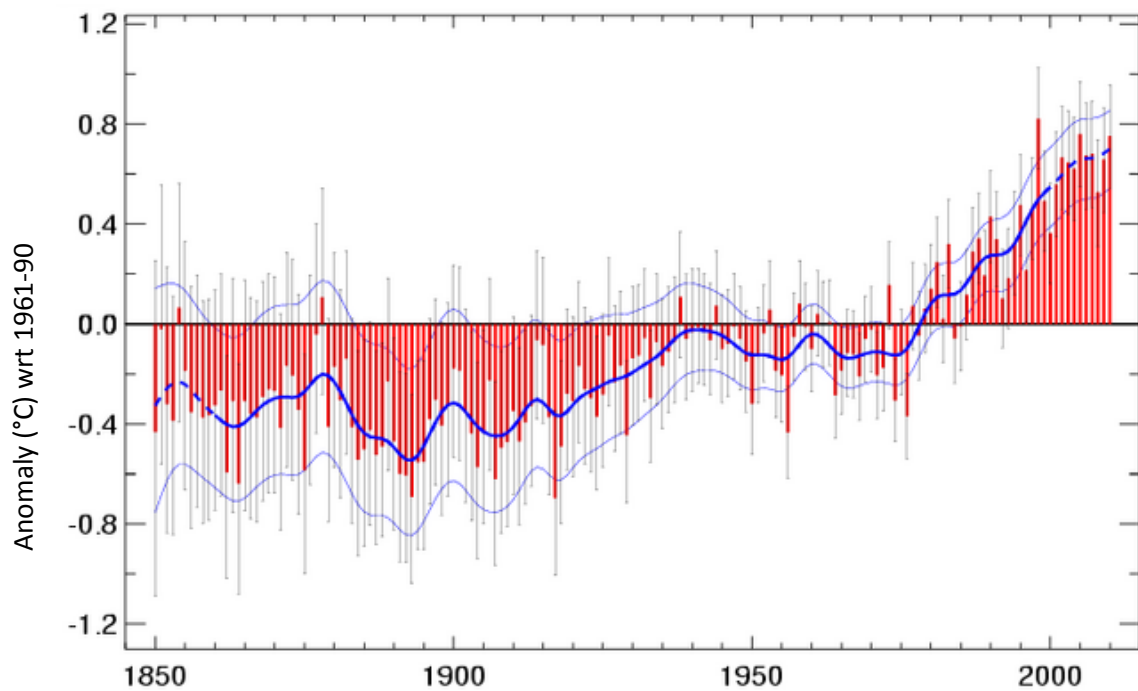


Figure 1.2. Global average land temperature 1850 – 2010 as a deviation from the average temperature from 1961 - 1990. Red bars indicate the annual average temperature and error bars indicate the 95 % confidence range. The dark blue line is the smoothed annual average and light blue lines indicate the 95 % confidence range. Source: [www.metoffice.gov.uk/hadbos](http://www.metoffice.gov.uk/hadbos)

As the mean global temperature is predicted to increase in the future, the areas of land suitable for peatlands may reduce due to changing temperature and precipitation (Marsden & Ebmeier 2012). The higher temperatures may result in drier peatlands with lower water tables, increased wildfires, biodiversity losses and cracking, erosion and flooding caused by increased heavy rainfall events (Tarnocai 2009, Pearce-Higgins *et al.* 2009, Marsden & Ebmeier 2012). Tarnocai (2009) modelled the impact of a 3 – 5 °C predicted increase in air temperature on peatlands in northern Canada. It was modelled that 60 % of the land area and 56 % of the organic carbon would be affected by climate change, resulting in a release of large amounts of carbon. Higher global temperatures are likely to increase soil temperature, alter water table depth and result in a longer growing season, which will impact on the carbon balance. The changes in CO<sub>2</sub> fluxes may depend on individual locations, as uptake may decrease in dry areas, but increase in wet areas. Similarly CH<sub>4</sub> fluxes may depend on specific sites, decreasing in drier areas, but possibly remaining the same or increasing in wet areas due to increasing temperatures. Higher CO<sub>2</sub>

concentrations may also result in higher concentrations of DOC within the ecosystem groundwater, however the export of DOC from the peatland is dependent on the fluvial export, therefore whether this carbon remains within the ecosystem or is lost will be dependent on factors such as precipitation (Strack 2008).

The increase in temperature has been linked to the anthropogenic emissions of greenhouse gases into the atmosphere. Greenhouse gases occur naturally within the atmosphere and include water vapour, CO<sub>2</sub>, CH<sub>4</sub>, nitrous oxide (N<sub>2</sub>O) and ozone (O<sub>3</sub>). Two of the most significant greenhouse gases are CO<sub>2</sub> and CH<sub>4</sub>, both of which are readily transferred between the land and atmosphere within peatland ecosystems. Peatlands can be either a sink or source for CO<sub>2</sub> and CH<sub>4</sub> depending on environmental conditions, such as water table depth. Changes in the concentration of CO<sub>2</sub> and CH<sub>4</sub> within the atmosphere can impact the amount of energy transferred from the earth into space by changing the amount of outgoing radiation absorbed by the gases. An increase in CO<sub>2</sub> and/or CH<sub>4</sub> concentrations would result in an increase in the amount of energy absorbed and therefore an increase in the heat retained by the earth atmosphere and surface. As seen in Table 1.1. CO<sub>2</sub> and CH<sub>4</sub> have different global warming potentials (GWP), an indication of their impact on global warming based on their absorption and longevity within the atmosphere. Therefore an identical increase in quantity of both gases would not have the same warming impact as each other, as CH<sub>4</sub> has a greater warming potential, especially over a short time period.

Table 1.1. The global warming potentials (GWP) of CO<sub>2</sub> and CH<sub>4</sub> in relation to CO<sub>2</sub>. (IPCC, 2007).

Gas	Lifetime in atmosphere (years)	Global warming potential (GWP)		
		20 years	100 years	500 years
Carbon dioxide (CO <sub>2</sub> )	5-20	1	1	1
Methane (CH <sub>4</sub> )	12	72	25	7.6

Due to the large amounts of carbon currently stored in peatlands there is a concern that any release of this carbon to the atmosphere could exacerbate global warming. Peatlands have been long term continuous sinks of carbon for millennia removing it from the atmosphere (Griffiths & Jarvis 2005). Although rates of primary production in peatlands can be small in comparison to other ecosystems, an accumulation of carbon still occurs due to low decomposition rates. Peatlands in a pristine state are typically thought to be a sink for CO<sub>2</sub> and a source of CH<sub>4</sub>, and overall a sink for carbon (Smith *et al.* 2004, Sottocornola & Kiely 2005).

Peatland soils can typically be split into three different layers, the acrotelm, the mesotelm and the catotelm. The acrotelm is the top layer of peat, which will usually be above the water table, or at least have sufficient air for active decomposition to occur. The mesotelm layer below the acrotelm is the area subjected to variations between aerobic and anaerobic conditions due to the movement of the water table. The catotelm layer is in between the mesotelm and mineral soil or rock below the peat and is permanently saturated with water and therefore subjected to anaerobic conditions (Clymo & Byrant 2008, Rydin & Jeglum 2006, Belyea & Malmer 2004).

There are a number of paths by which carbon moves between these layers and is gained or lost by peatlands as shown in Fig. 1.3. Many of these processes are dependent on the water table level, therefore whether they will occur in the acrotelm, mesotelm or catotelm will depend on the water table position at the time. These processes are common to most ecosystem types, however peatlands are distinct due to the sizes and relationship of the fluxes. Carbon in the form of CO<sub>2</sub> is taken up from the atmosphere by vegetation through photosynthesis. While alive, vegetation will respire and release CO<sub>2</sub> back into the atmosphere and soil. Once vegetation dies the carbon stored within the plants may follow a number of paths. Vegetation which is able to, will decompose on the surface and within the aerobic layers of peat and the carbon returned to the atmosphere or soil directly as CO<sub>2</sub>. Due to the ecosystem characteristics, such as anaerobic and acidic conditions, much of the vegetation will not quickly decompose and will enter anoxic layers, the mesotelm and catotelm. In these layers, in the absence of oxygen any carbon stored in vegetation will be broken down by microbes to form CH<sub>4</sub>, which will be released into the surrounding soil.

This gas can be released to the atmosphere through diffusion and in bubbles or transported to the surface through vegetation with aerenchyma (Greenup *et al.* 2000, Minkkinen & Laine 2006). Carbon can also be lost from peatland ecosystems in water runoff either in particulate or dissolved form as DOC, DIC and POC (Wieder & Vitt 2006, Rydin & Jeglum 2006).

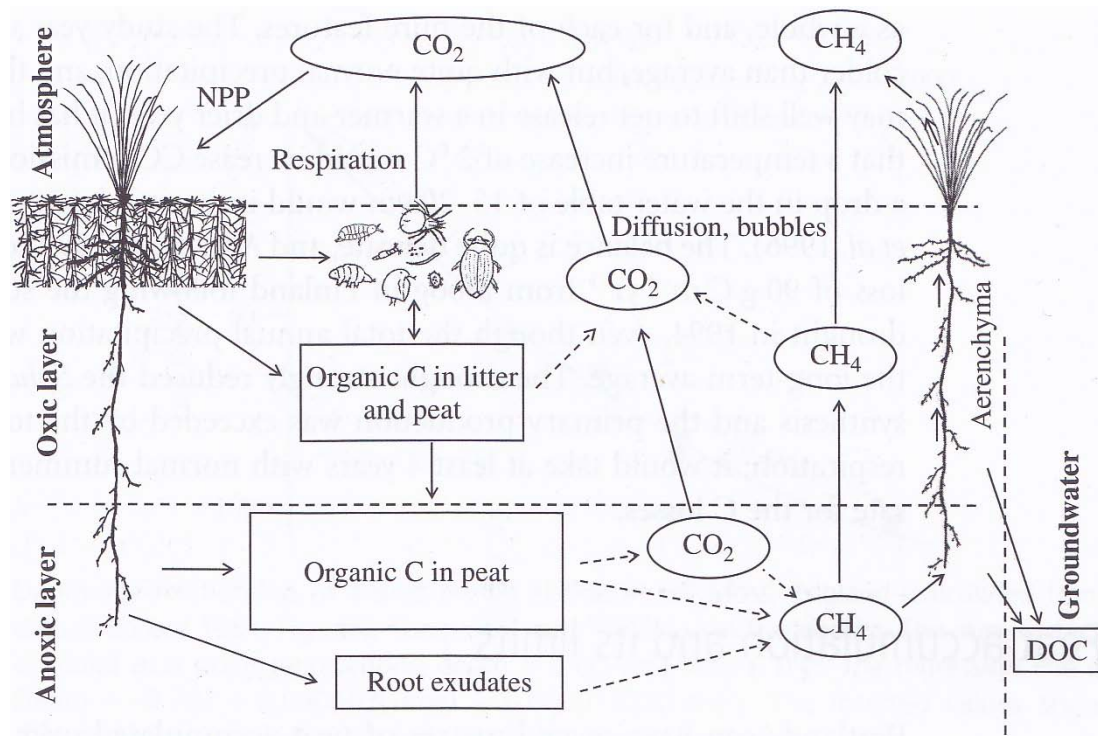


Figure 1.3. Diagram showing stores of carbon within peat soils and movement and losses of carbon between layers. The oxic layer will include the acrotelm and parts of the mesotelm that are above the water table level. The anoxic layer will include the catotelm and parts of the mesotelm below the water table level. Source: Rydin & Jeglum 2006.

In a healthy growing peatland ecosystem the inputs of carbon should exceed the losses, which leads to vertical growth of the peat column and an increase in the amount of carbon stored (Rydin & Jeglum 2006). It is estimated that approximately 5 – 15 % of the biomass produced in peatland systems becomes part of the anoxic layer (Clymo 1984, Gorham 1991, Parish *et al.* 2008). Where the oxic layer is too thick there may be limited or no peat accumulation due to new carbon inputs decomposing before reaching the catotelm (Belyea & Malmer 2004). Mature

peatlands may reach a point at which growth ceases as the inputs and losses of carbon balance each other out. This may be due to a reduction in the amount of carbon entering the ecosystem from vegetation growth or an increase in the amount of carbon being lost from the system. As the formed peat is in a constant state of decomposition, the ecosystem will require ongoing peat formation in order to balance out the losses of carbon to prevent the ecosystem from declining in size and carbon stored (Parish *et al.* 2008).

The rate of peat accumulation is dependent on the variation in climatic, hydrological and hydrochemical properties (Parish *et al.* 2008). Broad patterns indicate that accumulation is higher in nutrient poor peatlands as opposed to nutrient rich peatlands, oceanic peatlands rather than continental peatlands and equatorial peatlands as opposed to polar peatlands (Turunen & Tolonen 1996, Turunen *et al.* 2002, Parish *et al.* 2008). The Recent Rate of Carbon Accumulation (RERCA), which refers to the current rate of peat added to the system is estimated to be between 10 – 450 g C m<sup>-2</sup> y<sup>-1</sup> in boreal and temperate regions (Turunen & Tolonen 1996, Ohlson & Okland 1998, Mueller *et al.* 2003, Turunen *et al.* 2004), however these estimates do not take into account the losses of carbon from the anoxic layer. The Actual true net Rate of Carbon Accumulation (ARCA) takes into account these losses and has been estimated by Clymo *et al.* (1998) to be 21 g C m<sup>-2</sup> y<sup>-1</sup>. Tolonen & Turunen (1996) suggested that the ARCA could be estimated to be two thirds of the Long-term apparent Rate of Carbon Accumulation (LORCA), which estimates the rate of accumulation over the long term by looking at the carbon mass in a peat column in relation to the number of years the column took to form. Rates of LORCA have been estimated between 10 – 40 g C m<sup>-2</sup> y<sup>-1</sup> in boreal and temperate zones (Turunen *et al.* 2002, Clymo *et al.* 1998, Turunen *et al.* 2004).

As seen in Table 1.1. the impact of CH<sub>4</sub> on global warming is more significant than equivalent levels of CO<sub>2</sub>. Globally, wetlands are the largest source of CH<sub>4</sub>, releasing up to 45 % of global methane emissions (Segers 1998) and northern peatlands are estimated to be responsible for 9.8 % of the wetland CH<sub>4</sub> emissions (Bartlett & Harriss 1993). The net CH<sub>4</sub> exchange between the land and atmosphere is dependent on the balance between two microbial processes, methanotrophy and

methanogenesis, the consumption and production of CH<sub>4</sub> respectively (Le Mer & Roger 2001), which are influenced by temperature, vegetation, water table position and peatland chemical characteristics (Blodau 2002). A range of microbes named methanogens are responsible for producing methane under anaerobic conditions (Charman 2002). Three stages of microbial processes on vegetation are required before the methanogens are able to use the compounds; the conversion of biological polymers to monomers by hydrolytic microflora, acidogenesis by fermentative microflora to form volatile fatty acids, organic acids, alcohols, H<sub>2</sub> and CO<sub>2</sub>, and finally acetogenesis by syntrophic or homoacetogenic microflora (Le Mer & Roger 2001). Once these three stages are complete methanogens are able to use the substrates to produce CO<sub>2</sub> and CH<sub>4</sub>. These four stages of methanogenic fermentation convert the plant material to CO<sub>2</sub> and CH<sub>4</sub> as seen in equation 1.2. As most methanogenesis takes place within the anoxic layer, the actual production of CH<sub>4</sub> may not be reflected in measured surface fluxes, as the release of CH<sub>4</sub> will depend on transportation to the surface, which is influenced by diffusion, ebullition and plant aerenchyma (Greenup *et al.* 2000).



The converse process, methanotrophy, involves the oxidation of CH<sub>4</sub> to form CO<sub>2</sub> by methanotrophic bacteria. In order to occur it requires aerobic conditions, so below the water table level activity is inhibited, or at least limited to areas where there are pockets of air remaining. Two distinct forms of CH<sub>4</sub> oxidation have been identified in soils, firstly high affinity oxidation which occurs at CH<sub>4</sub> levels lower than 12 ppm and the second, low affinity oxidation, which occurs at concentrations above 40 ppm. Methanotrophs can oxidise 70 – 90 % of methane produced by methanogens and are often clustered around areas of high CH<sub>4</sub> (Le Mer & Roger 2001), therefore the methanotroph activity is key in determining net flux rate. Methanotrophic rates are largely dependent on water table position as this will determine the amount of oxygen available to the microbes to oxidise CH<sub>4</sub>.

The future environment is predicted to have higher atmospheric concentrations of CO<sub>2</sub> and on average be warmer with altered weather patterns (Wu *et al.* 2011, Piao *et al.* 2012, Cao & Woodward 1998). A large amount of the carbon stores are in high latitude soils (Qian *et al.* 2010, Koven *et al.* 2009), partly due to lower levels of ecosystem respiration as a result of lower temperatures (Davidson & Janssens 2006). Therefore a global increase in temperature and the greater warming projected at higher latitudes may result in increased respiration and a release of CO<sub>2</sub> into the atmosphere (Knorr *et al.* 2005). However conversely, an increase in available CO<sub>2</sub> and warmer temperatures may result in an increase in NPP, which could counter increased respiration (Wu *et al.* 2011, Piao *et al.* 2012).

Some predictions indicate extended drought periods due to climate change and laboratory experiments suggest increased drought conditions may change the hydrology of peatlands (Holden & Burt 2002). This is of particular concern to peatland ecosystems as so much of their functioning is due to the high water tables inhibiting decomposition of dead vegetation. A lowering of the water table due to drought would increase the amount of oxygen available to microbes to decompose the carbon stored within the peat column (Rydin & Jeglum 2006).

Many peatland ecosystems across the UK can no longer be considered to be in a pristine state due to anthropogenic impacts upon them. Williams (2006) reported that only 54 % of blanket bogs and 21 % of lowland bogs in the UK were considered to be in a favourable condition. The adverse activities identified as the most significant included over-grazing, burning, water management, invasive species, a lack of remedial management, agricultural activity and pollution. These factors may have resulted in altered vegetation communities, hydrology and microbial activity within peatlands. As peatland ecosystems form around specific environmental criteria such as high water tables, low nutrients and low temperatures, their functioning is vulnerable to environmental changes. The damage to the ecosystem could result in the local extinction of flora and fauna as well as the failure of ecosystem services such as carbon storage or hydrological controls. In addition, if peatland ecosystems are already stressed due to human activities, then they may be more vulnerable to

additional stress in the future, such as periods of drought or increasing temperatures (Rydin & Jeglum 2006).

Peatlands that have been drained and turned over to grassland for agriculture have been estimated to lose between 2.5 – 3.5 tC ha<sup>-1</sup> y<sup>-1</sup> (Joosten & Clarke 2002, Schipper & McLeod 2002). In addition farming practices such as ploughing expose peat soils to the air, stimulating decomposition and soil that is left bare may be lost due to erosion by wind and water (Joosten & Clarke 2002, Holden *et al.* 2006b). Grazing by agricultural livestock can result in peat loss due to vegetation and soil damage caused by the animals and increases in organic sediments in lakes in Ireland have been linked to increased sheep numbers (Evans 1997, Huang & O'Connell 2000, Holden *et al.* 2006b, McHugh *et al.* 2002). Large areas of UK uplands are part of estates managed for grouse shooting. These areas are often burned periodically to stimulate fresh heather growth that the grouse require. This burning has been found to reduce the carbon accumulation of peatlands and if the burning is not controlled properly it can result in the removal of all of the surface vegetation (Garnett *et al.* 2000, Holden *et al.* 2006b).

Numerous peatlands in the UK have been drained to allow the establishment of forestry plantations. This forestation can result in the exposure of the soil to oxygen, lower soil temperatures and lower pH levels, which may affect the CO<sub>2</sub> emissions from the soil (Rydin & Jeglum 2006, Silvola *et al.* 1996, Laine *et al.* 1995). While the biomass and carbon store increase beyond the original ecosystem store as a result of tree growth, when the trees are felled the ecosystem carbon store will be lower than before due to losses from the peat (Parish *et al.* 2008).

Peat is considered useful as a source of fuel and horticultural material due to its carbon content and physical properties. Consequently there are many peatlands where peat is harvested from the ground for human uses. This can result in 50 kg C m<sup>-3</sup> being removed in the peat harvested from a site (Parish *et al.* 2008). Once peat has been removed, the carbon stored in it may be released to the atmosphere if it is burned as fuel, or decompose if used where it is exposed to air. The methods used to harvest peat may add to carbon loss as peat is milled and left in stacks to dry. The unvegetated soil surface is also vulnerable to water and wind erosion, leading to

further carbon loss (Holden *et al.* 2006b, Cleary *et al.* 2005, Waddington *et al.* 2002).

The current impact of management practices and environmental degradation upon the carbon fluxes of peatlands are not fully understood. It is thought that degraded peatlands could be releasing  $3 \text{ Gt y}^{-1}$  of  $\text{CO}_2$  to the atmosphere, roughly equivalent to 10 % of the anthropogenic emissions of 1990 (Parish *et al.* 2008). The overall status of UK peatlands as a sink or a source of carbon is not known. It is therefore important to understand what impact different management practices will have on stored peatland carbon and whether peatlands are exacerbating global warming by releasing stored carbon or are a part solution by still acting as a sink for atmospheric carbon. At the Sixth Conference of Parties to the United Nations Framework Convention on Climate Change it was decided that carbon sequestration activities such as crop land revegetation and forest management could be used by countries to meet their emissions targets (UNFCCC 2001). As a result, quantifying the impact of peatland management practices on carbon exchange will provide landowners and policy makers with an additional tool for meeting emissions targets by proactive management of peatlands in order to increase the amount of carbon they sequester annually.

## 1.2 Aims

This thesis aims to improve knowledge about peatland processes related to carbon exchange. It aims to consider specific issues that may have led to a degradation of peatland ecosystems, such as drainage and nitrogen deposition, as well as considering the overall status of UK peatland ecosystems. This thesis tests the following hypotheses through the use of field experiments.

- It is hypothesised that increasing levels of nitrogen deposition will result in increased vegetation biomass and increased net ecosystem exchange (NEE). This is due to the fact that ombrotrophic peatland vegetation growth is believed to be inhibited by limitations in the nutrients available to vegetation.
- It is hypothesised that peatland open drains reduce the water table depth in proximity to them, reducing CH<sub>4</sub> emissions and increasing CO<sub>2</sub> emissions. It is therefore hypothesised that blocking drains will reverse these effects as CO<sub>2</sub> and CH<sub>4</sub> cycling within peatland ecosystems is expected to be largely dependent upon water table levels.
- It is hypothesised that annually an undisturbed peatland will be a sink for CO<sub>2</sub> and a source of CH<sub>4</sub> due to high water tables and unmanaged vegetation at the site. It is hypothesised that CO<sub>2</sub> fluxes will exceed CH<sub>4</sub> fluxes and the peatland will be a sink for carbon.
- It is hypothesised that non destructive vegetation surveying can be used to estimate vegetation biomass and leaf area index (LAI) and subsequently net ecosystem exchange (NEE).

## 1.3 Overview of thesis

This study involves fieldwork at three different peatland sites in the UK to investigate the hypotheses in section 1.2 examining different aspects of peatland carbon exchange.

The first chapter provides a broad introduction to peatland ecosystems and their importance as global carbon stores in relation to global warming. As some of the methods used for fieldwork measurements were similar across sites, Chapter Two gives a detailed description of the use of these methods. This includes measurements of water table, Net Ecosystem Exchange (NEE), Ecosystem Respiration (ER) and methane (CH<sub>4</sub>) flux measurements. At individual sites, there were specific variations to the methods and the specific details of how the methods were used are addressed in the chapters relating to that site.

Chapter Three involves measurements of the NEE and ER at a site where additions of nitrogen have been made over a number of years. The chapter investigates whether there is any impact of nitrogen addition on NEE or ER. In addition, the usefulness of a method to calculate the biomass and leaf area index of vegetation without the need to destructively harvest the vegetation was investigated. Chapter Four examines the impact of peatland restoration by blocking open drains on the carbon balance. A field site that was historically drained was investigated prior to and post blocking to identify the impact of the restoration work on the carbon balance at the site. Chapter Five investigates the annual carbon balance of an undisturbed peatland in the UK using continuous NEE measurements and chamber measurements of CH<sub>4</sub>. Measurements from studies at other field sites are included to compare the peatland to other sites across the UK and worldwide. Chapter Six summarises the work included here and discusses possible further work to improve our knowledge of peatlands.

## **CHAPTER 2**

### **METHODS AND MATERIALS**

## **2.1 Methods**

A number of the methods used for making measurements such as water table depth and chamber flux measurements were common to more than one chapter and therefore these are described in detail in this chapter. Where there are variations in how the method was applied at specific sites, these are discussed in the relevant chapter methods section.

## **2.2 Water table measurements**

Water table measurements were made using piezometers as used in previous studies (Burt *et al.* 2002, Lilly 1999, Pfeiffer *et al.* 2006). At locations where water table was to be measured a dipwell was permanently installed as shown in Fig. 2.1. Dipwells consisted of 40 mm diameter PVC piping that was cut to approximately 1 metre in length. The bottom end of the pipe was sealed using duct tape to prevent the ingress of soil when it was inserted into the ground. Along the length of the pipe every 50 mm, two 4 mm diameter holes were drilled on opposite sides to each other. This allowed water to enter the pipe so that the water level within the pipe matched that in the surrounding soil. On top of the dipwell either a rubber bung or plastic end cap was fixed to prevent rain water from entering the pipe. Dipwells were inserted into the ground until approximately 15 cm of the pipe remained above the soil surface. Once inserted into position the distance from the soil surface to the top of the dipwell was measured so that water depth measurements within the dipwell could be related to the soil surface.



Figure 2.1. A dipwell (left) and flux chamber base (right), which were left in position permanently in between measurements.

This design of dipwell could be used for manual measurements using a tape measure to measure the distance of the water from the top of the dipwell, or automated water table measurements using a pressure sensor to determine the water table depth. Manual and automated measurements were both used in experiments in this thesis, using tape measures for manual measurements and PDCR 1830 pressure transducers (Campbell Scientific) for automated measurements. Details of their specific use is given in individual chapters. When dipwells were inserted into the soil, the height of the top of the dipwell above the soil was measured as represented by Arrow A in Fig. 2.2. For manual measurements a tape measure was used to measure the distance of the water level below the top of the dipwell as represented by Arrow B. The height of the dipwell above the soil surface (Arrow A) was subtracted from the depth of the water level below the top of the dipwell (Arrow B) to give the depth of the water table below the soil surface. For automated measurements the entire length of the dipwell was measured prior to insertion into the soil as represented by Arrow C in Fig. 2.2. The pressure transducer measured the height of water above the sensor, represented by Arrow D in Fig. 2.2. The height of Arrow D was subtracted from the height of Arrow C to give the depth of the water table below the top of the dipwell.

The height of the dipwell above the soil (Arrow A) was then subtracted from this depth in order to give the depth of the water table below the soil surface.

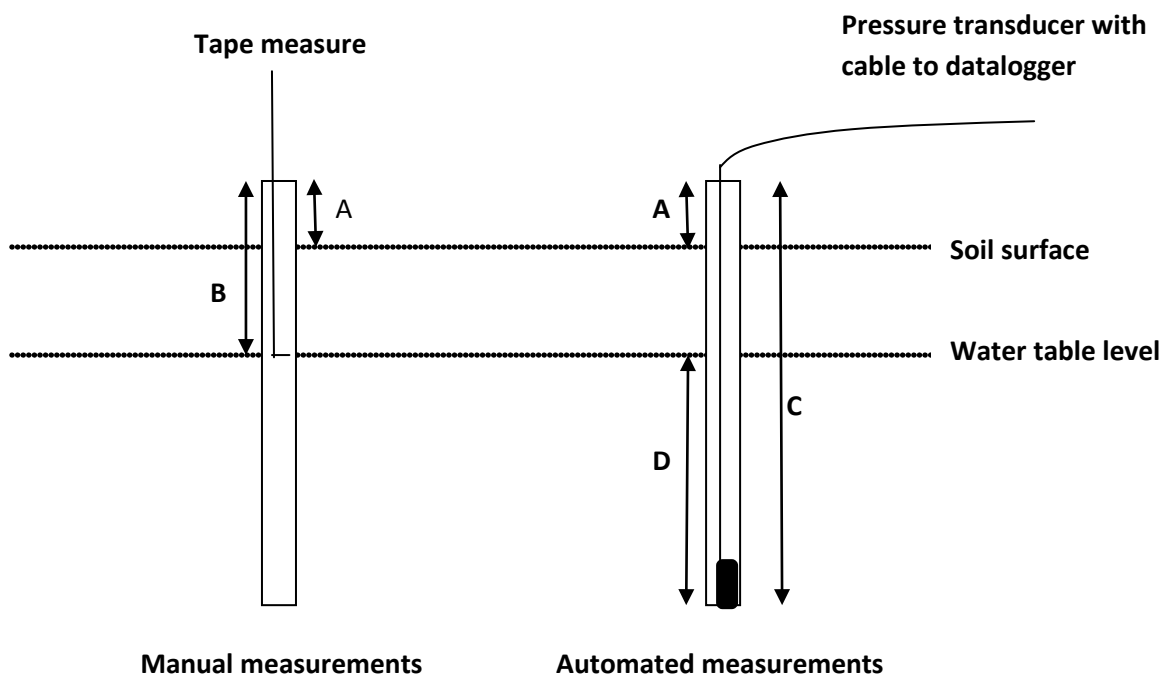


Figure 2.2. Schematic diagram of the arrangement used for manual and automated water table measurements. Arrow A represents the height of the top of the dipwell above the soil surface, Arrow B represents the distance of the water table below the top of the dipwell, Arrow C represents the dipwell length and Arrow D represents the height of the water level above the pressure transducer.

## 2.3 Flux chamber base

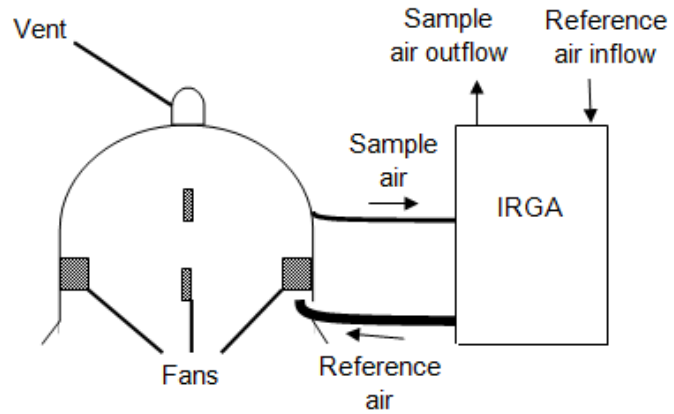
In order to measure gas fluxes of CO<sub>2</sub> and CH<sub>4</sub> between the ground and atmosphere over specific sections of ground, flux chambers were used as described in (Jensen *et al.* 1996, Livingston & Hutchinson 1995, Tuittila *et al.* 2000). The measurements for both gases required two sections to create the flux chamber, a base surrounding the ground surface area and a chamber lid that enclosed the flux chamber headspace. As seen in Figs. 2.3 and 2.4. the chamber base could be used for both CO<sub>2</sub> and CH<sub>4</sub> measurements depending on the chamber lid attached to the base.

The base consisted of PVC pipe 0.4 m in diameter and 0.2 m in height with a joining flange screwed to the top of the pipe and sealed using silica sealant. These bases

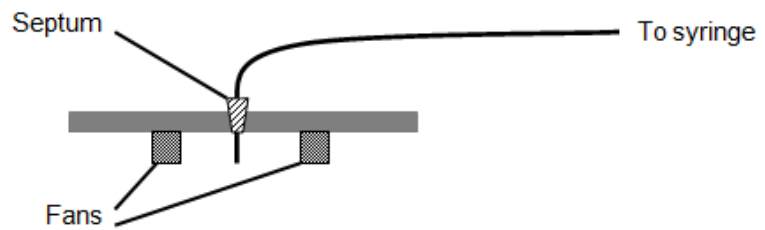
were permanently left in place at the sites and dug into the ground to provide as good a seal as possible, without cutting vegetation shoots and roots passing underneath the edge of the chamber base.

However there was a compromise to be made between sealing the chamber base and damaging the vegetation and soil (Heinemeyer *et al.* 2011). To ensure that accurate flux measurements are made it is necessary to seal the chamber base to the soil as well as possible to prevent gaps through which heightened gas concentrations within the headspace may diffuse to the atmosphere and lead to inaccurate fluxes. However, in peatlands, sealing the chamber well in the soil may require the cutting of roots for species such as *Calluna vulgaris* which have roots covering large horizontal distances, potentially killing or damaging the vegetation and affecting the CO<sub>2</sub> flux. As the insertion of the chamber leads to an “edge effect” where the rim of the chamber is entered into the soil, the use of a large diameter chamber base for flux measurements reduced the ratio between the circumference of the chamber and the chamber surface area, reducing the impact of an edge effect upon the flux measurements (Yiqi & Zhou 2006, Kutsch *et al.* 2010).

A – Open chamber lid



B – Closed chamber lid



C – Flux chamber base



Figure 2.3. A diagram showing the components involved in gas flux measurements. Diagram A is the chamber and analyser for use measuring CO<sub>2</sub> fluxes. Diagram B shows the chamber lid used for measuring CH<sub>4</sub> fluxes in a closed chamber. Diagram C is the chamber base, which was used for both CO<sub>2</sub> and CH<sub>4</sub> fluxes, along with lid A and B respectively.

## 2.4 CO<sub>2</sub> chamber flux measurements

CO<sub>2</sub> fluxes were predominantly measured using a chamber method to allow comparisons between experimental treatments. The three most frequently used flux chamber methods are closed-static, dynamic-closed and open chambers (Norman *et al.* 1997).

Closed-static chambers consist of a chamber headspace from which regular gas samples are taken over a period of time. These samples are then analysed in a laboratory to determine the gas concentrations within the sample and from this a flux rate is determined. Dynamic-closed chambers also involve a closed headspace, however air is circulated between the chamber and a connected gas analyser. The gas concentration is analysed continuously from which the flux rate is determined. Open-chambers circulate atmospheric air through the chamber headspace and sample the gas concentration in the atmospheric and chamber air. The difference of the gas concentration between the atmospheric and chamber air is measured and combined with the flow rate to determine the flux (Norman *et al.* 1997).

Measurements of CO<sub>2</sub> were made using an open system chamber method, as this results in smaller estimation errors than closed systems and would avoid high concentration levels in the chamber headspace (Pumpanen *et al.* 2004, Fang & Moncrieff 1996). A Control Interface Module (CIM), containing an integrated Infra-Red Gas Analyser (IRGA) (PP systems) was used to measure the fluxes. Reference atmospheric air was pumped into the chamber and the flow rate measured by a mass flow sensor. The analyser is capable of producing flow rates of up to 80 L min<sup>-1</sup>, however flow rates of between 30 – 40 L min<sup>-1</sup> were typically used for measurements, as high flow rates in or out of a chamber can result in an increase or decrease of pressure within the chamber headspace, which can enhance or suppress the gas flow between the soil and atmosphere (Fang & Moncrieff 1996).

The IRGA consists of a single infra red source and sensor and the air being analysed was switched between the reference air and chamber analysis air by a solenoid valve. The CO<sub>2</sub> concentration of the reference air was averaged over 30 seconds after which the solenoid valve switched to the analysis air for a further 30 seconds. The

averages of the two 30 second periods are used to determine the difference in CO<sub>2</sub> concentration between the reference air and the sample air.

The flux is calculated using the following formula:

$$\text{CO}_2 \text{ flux } (\mu\text{mol m}^{-2} \text{ s}^{-1}) = \Delta C \times \frac{V}{A} \times 7.43583 \times 10^{-3} \quad (2.1)$$

Where  $\Delta C$  is the difference in CO<sub>2</sub> concentration in PPM between the reference and sample air,  $V$  is the flow rate of reference air into the chamber in ml minute<sup>-1</sup> and  $A$  is the ground surface area of the chamber in m<sup>2</sup>. The constant relates to the volume occupied by one mol of gas at standard temperature and pressure.

Net Ecosystem Exchange (NEE) is a measurement of the net exchange of CO<sub>2</sub> entering and leaving the ecosystem. The net figure is derived from the balance between Gross Primary Productivity (GPP), the uptake of CO<sub>2</sub> through vegetation photosynthesis and the release of CO<sub>2</sub> through Ecosystem Respiration (ER) from flora and fauna.

Chambers originally provided with the analysers to measure NEE were found to be insufficient in height and diameter to be used with the vegetation present at the sites. A set of larger chambers were therefore constructed to be compatible with the analysers and the chamber bases already in use at some field sites, which helped limit any edge effect on the measurements. For the chamber lid a large Victorian bell cloche, diameter 45 cm, height 36 cm (Haxnicks Ltd) made from transparent injection-moulded polystyrene was modified to fit to the chamber base and attach to the CIM. The top of the cloche had a 50 mm diameter hole drilled into it to allow a vent to be added, which helped to minimize pressure changes caused by the inflow and outflow of air from the reference and sample air gas lines. On the inside of the chamber four 12 V, 50 x 50 x 15mm Maglev Axial Fans (RS components) were inserted to aid the mixing of the chamber air and to assist preventing condensation on the inside of the chamber. Each fan had a flow rate of 21 L/min. Tubing was added for the reference air to be pumped into the chamber and analysis air to be sampled from the chamber. A 109 temperature probes (Campbell scientific Ltd) was

also installed inside the chamber to check the chamber temperature did not deviate too much from the air temperature.

In order to be able to measure ER using the CIM, a modified chamber was constructed. This allowed one analyser to make ER measurements at a field site while the remaining analysers were making NEE measurements at the site at the same time. This modified chamber consisted of a standard chamber design modified to prevent the vegetation being exposed to any light. A black painted layer was added to the inside of the chamber and on the outside a layer of duct tape was added to further increase the darkening effect. Finally a layer of aluminium foil was added on top of the duct tape, partly to add a further layer to prevent light ingress, but additionally to reflect sunlight to prevent the chamber temperature increasing and influencing the measurements.

Each CIM had a CR200 datalogger (Campbell scientific Ltd) attached to it, which logged the chamber temperature and soil temperature using 109 temperature probes (Campbell scientific Ltd) whilst the CO<sub>2</sub> flux measurements were taking place. Separate dataloggers and sensors were used to measure the air temperature and PAR whilst CO<sub>2</sub> flux measurements were being made. Alongside each chamber base was a dipwell consisting of a 1 m long, 40 mm diameter pvc tube with 4 mm diameter holes drilled every 5 cm down the length of the tube. This was used to measure the depth of the water table from the soil surface when measurements were made.



Figure 2.4. Photographs of flux measurements in progress for closed chambers measuring  $\text{CH}_4$  (left) and an open system chamber and CIM for  $\text{CO}_2$  (right).

## 2.5 $\text{CH}_4$ flux measurements

Measurements of  $\text{CH}_4$  fluxes were made using a closed chamber method as described in Livingston & Hutchinson (1995). The chamber bases were the same used for the  $\text{CO}_2$  flux measurements as described in section 2.3. The chamber lid consisted of an octagonal sheet of aluminium 0.4 m across with an 11 mm circular hole drilled in the centre of a lid. A 0.4 m diameter circle of EPDM P-section draught excluder (RS components) was attached to the underside of the lid to create a seal between the lid and base while measurements were taking place. Lids were held in place by four 12 mm bulldog clips. On the underside of the lid were two 12 V, 50 x 50 x 15mm Maglev Axial Fans (RS components) attached to the lid with Velcro. These were each powered by a 160mAh NiMH PP3 9V battery (RS components) which produced a flow rate of 9.7 L/min. An 11 mm plug diameter stopper turnover flange (Fisher Scientific UK Ltd) was inserted into the hole drilled into the lid and attached to this was a 1.5 m length of Tygon tubing, formulation R-3603, inner diameter 1.6 mm, outer diameter 4.8 mm (Saint-Gobain Performance Plastics). On the end of this tubing was a 3 way tap with a 20 ml syringe and needle attached (Fisher Scientific UK Ltd).

When making measurements the fans were switched on before the lid was fastened to the chamber base. Prior to a sample being taken the syringe and Tygon tubing was flushed twice with air from the chamber to ensure that when the sample was taken it consisted of chamber air rather than the air in the Tygon tubing. The sample of air was then injected into an evacuated 20 ml clear glass vial with an aluminium crimp top and PTFE/rubber seal (Fisher Scientific UK Ltd). The first gas sample was taken immediately after the chamber lid was attached and further samples were taken approximately every 20 minutes until 5 samples had been collected. This gave an enclosure time of approximately 80 minutes which was determined to be sufficient for a detectable increase in gas concentration to occur at the sites in use, without chamber concentrations rising too high. Having five gas samples for each chamber measurement allowed individual samples to be rejected if there was suspicion they were inaccurate, without compromising the flux calculations.

The samples were analysed on an HP5890 Series II gas chromatograph (GC) (Hewlett-Packard) using a flame ionisation detector (FID). The vials and seals were chosen as they are sufficient to store samples for several months, however samples were usually analysed within 72 hours of being collected in the field. Standard gases of 1.26, 1.8, 5.04 and 100.9 ppm +/- 1 % (BOC Industrial Gases UK) were used to calibrate the GC output for each run and compensate for drift. A linear regression of the standards known gas concentration and GC peak area output was used to calculate the gas concentrations within the samples. Once the concentrations had been calculated the results were manually checked to identify any individual samples that had concentrations that were not consistent with the other samples from the same measurement plot. In the field, vials that did not appear to have maintained a vacuum were noted. When gas concentrations had been determined from the GC, the samples from individual plots were plotted against sample time and samples that were not consistent with the other samples were discarded. Taking five samples of air per measurement plot provided resilience for when individual samples had to be discarded. Vials that were found to repeatedly have errors were replaced to reduce the number of samples being rejected during measurements.

A flux chamber measurement will typically yield a response in concentration over time as seen in Fig. 2.5. As gas moves from the soil into the atmosphere (the flux chamber headspace during measurements) the concentration of the gas will increase over time. The gradient of the regression applied to the sample measurements is used to determine the rate at which the gas passes from the soil to atmosphere. While Fig. 2.5. shows a linear relationship between the gas concentration and enclosure time, once the gas concentration within the flux chamber headspace rises, the flux rate may decrease due to the diffusion of the gas from the headspace into the soil. Therefore measurement plots with high fluxes may experience a reduction in the flux rate over time if the enclosure time is too long as the difference between headspace and soil concentration decreases. The flux is calculated using the equation 2.2:

$$\text{CH}_4 \text{ flux } (\mu\text{mol m}^{-2} \text{ s}^{-1}) = \frac{\Delta C}{\Delta t} \cdot \frac{p V}{A} \quad (2.2)$$

where  $\Delta C / \Delta t$  is the rate of concentration change ( $\mu\text{mol mol}^{-1}$ ) over time ( $t$ , seconds),  $p$  is air density in  $\text{mol m}^{-3}$ ,  $V$  is the volume of the chamber headspace in  $\text{m}^3$  and  $A$  is the ground surface area covered by the chamber in  $\text{m}^2$ .

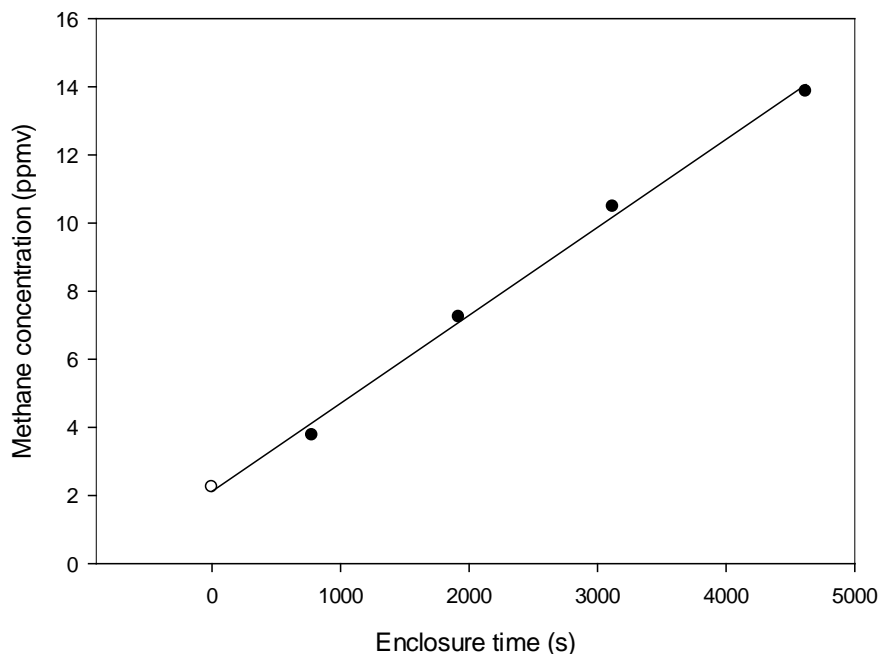


Figure 2.5. Plot of gas samples from a closed chamber showing methane concentration increasing during the enclosure time.

The time before the flux rate ceases to be linear will depend on the flux rate and the volume of the chamber, however it has been suggested that a linear relationship may end within 4 minutes of the start of measurements (Fang & Moncrieff 1996, Kroon *et al.* 2008, Nakayama 1990). If a linear regression is used to calculate the fluxes it has been estimated that the flux could be underestimated by 35 – 40 % (Pumpanen *et al.* 2004, Kutzbach *et al.* 2007). For flux measurements that do not align satisfactorily with a linear response, it has been shown that a nonlinear regression may improve the fit (Kroon *et al.* 2008). In order to fit the most appropriate method to the data, for each flux measurement the five methods shown below from Levy *et al.* (2011) were applied to the samples.

### 1. Linear regression

This method fitted a standard line of best fit through the observations using the following equation:

$$C_t = a + b \times t. \quad (2.3)$$

The value  $C_t$  represents the gas concentration at the specified time,  $a$  is a constant equivalent to the starting gas concentration,  $b$  is the gradient of the regression and  $t$  is the specified time.  $\Delta C / \Delta t$  is equal to value  $b$  in the regression.

### 2. HM model

This method uses a negative exponential curve to create a non-linear model using the equation below:

$$C_t = C_{\max} - (C_{\max} - C_0) \exp(-kt) \quad (2.4)$$

The value  $C_t$  represents the gas concentration at the specified time,  $C_{\max}$  is the concentration value at equilibrium,  $C_0$  is the starting gas concentration,  $k$  is a constant and  $t$  is the specified time.

In order to determine the change in concentration over time the following equation is used:

$$\Delta C / \Delta t_0 = k(C_{\max} - C_0) \quad (2.5)$$

### 3. Non-steady-state diffusive flux estimator (NDFE)

NDFE is a model to account for non-steady-state conditions and uses a square-root curve. The change in the gas concentration over time is given by the equation 2.6:

$$C_t = C_0 + (f_0\tau(1/h))(2\sqrt{(t/\tau)/\pi} + \exp(t/\tau) \operatorname{erfc}(\sqrt{t/\tau}) - 1) \quad (2.6)$$

The value  $C_t$  represents the gas concentration at the specified time,  $C_0$  is the starting gas concentration,  $\tau$  is a time constant,  $h$  is the effective chamber height (volume/area),  $\operatorname{erfc}$  is the complementary error function and  $f_0$  is the flux at  $t = 0$ .

### 4. Intercept method

This method avoids non-linear models by calculating the gradient ( $= \Delta C / \Delta t$ ) for each successive pair of measurements. A linear regression is then carried out on the previous regressions against time:

$$\Delta C / \Delta t_{\text{pred}} = a + b \times t \quad (2.7)$$

Where  $b$  is the gradient of the second regression,  $t$  is the time and  $a$  equals the flux rate at enclosure time zero. The rate of concentration change is therefore obtained from value  $a$ .

### 5. Asymptotic regression

This method was a similar non-linear fit to the HM model, but is more robust and will fit a linear line where the data are linear. The fit is made with the following equation:

$$C_t = a + b \times k^t \quad (2.8)$$

The value  $C_t$  represents the gas concentration at the specified time,  $a$  and  $k$  are constants,  $b$  is the gradient of the regression and  $t$  is the specified time. The change in concentration over time is calculated using the following equation:

$$dC/dt = \ln(k) \times b \quad (2.9)$$

Each of these methods was applied to each individual measurement plot. Once this had been done, all five methods were compared manually and the method that had the best fit and accounted for the majority of the variance was selected for use.

## **CHAPTER 3**

### **THE IMPACT OF NITROGEN DEPOSITION ON CO<sub>2</sub> FLUXES FOR AN OMBROTROPHIC BOG**

### 3.1 Introduction

Ombrotrophic peatlands are defined as those that receive all of their inputs from precipitation and airborne particles, unlike minerotrophic peatlands which also receive nutrients through groundwater flow (Rydin & Jeglum 2006). As a result, the nutrients inputted into the ecosystem are limited and therefore the quantity of nutrients available for vegetation to utilise is low (Wieder & Vitt 2006). In peatland ecosystems the growth of plants is most commonly limited by nitrogen, phosphorus and potassium, but primarily nitrogen (Hayati & Proctor 1991, Hoosbeek *et al.* 2002). This makes them the most sensitive of peatland ecosystems to external nutrient additions as the ecosystem is adapted to a low nutrient state (Rydin & Jeglum 2006).

Nitrogen is one of the most common elements on the earth, however much of it is unavailable to most organisms in the relatively inert form  $N_2$ , which makes up around 75 % of the atmospheric mass and 99.96 % of the total amount of nitrogen within the earth (Vitousek *et al.* 1997, Scharenbroch & Lloyd 2004, Atkinson 2000). Only 0.0026 % of global nitrogen is in a form that vegetation is able to utilise, such as ammonium, ammonia, nitrate and nitrogen dioxide (Scharenbroch & Lloyd 2004, Dittman *et al.* 2007). It is the availability of these compounds of nitrogen and their movement within the nitrogen cycle by atmospheric deposition, fertilisation and fixation that impacts upon vegetation growth (Jones & Willett 2006, Scharenbroch & Lloyd 2004).

There are five main processes by which nitrogen is transported and transformed within the nitrogen cycle. Nitrogen fixation involves the transformation of  $N_2$  from its inert form into compounds that plants are able to utilise by microorganisms. During assimilation, plants convert nitrate, nitrite and ammonium ions into organic nitrogen compounds used within the plant structure. Mineralisation is the process where organic nitrogen is degraded by bacteria or fungi and ammonium is released. Nitrification is carried out by two sets of bacteria to oxidise ammonia into nitrite and then oxidise the produced nitrite into nitrate. Denitrification occurs when denitrifying bacteria reduce nitrates into  $N_2$  and release it into the surrounding soil and atmosphere.

Vegetation found in ombrotrophic peatlands is typically long lived and adapted to conserve the nutrients available for growth. Most plants grow leaves over the course of a single growing season, however some species of peatland vegetation such as *Erica* spp and *Empetrum* spp retain leaves over a number of years. To cope with this length of time and low winter temperatures, leaves will have adaptations that make the leaf narrow, stiff or leathery. This limits the ability of the plant to photosynthesise, but requires a limited amount of nitrogen within the leaf and does not require repeated acquisition of nitrogen to grow new leaves every year, allowing the vegetation to cope in a nutrient poor environment (Rydin & Jeglum 2006).

*Sphagnum* spp have developed methods to secure the nutrients they require in the deficient environment of a bog and are very efficient at using these nutrients. Their efficiency with the limited nutrients means that very often they are able to outcompete vascular plants (Clymo & Hayward 1982, Wiedermann *et al.* 2009, Fritz *et al.* 2012). *Sphagnum* spp are able to accumulate nitrogen through chlorophyllous cells (Clymo & Hayward 1982) and can transfer nutrients from their deteriorating vegetation to the growing sections (Aldous 2002). *Sphagnum* spp are also able to utilise a significant proportion of nitrogen that has been fixed by microbes, although this may not make up a large proportion of the total nitrogen used by *Sphagnum* spp due to the restraints of acidity and oxygen availability on microbial activity (Aldous 2002, Berg *et al.* 2013). Although *Sphagnum* spp are very effective in low nutrient conditions, when they are exposed to high levels of nitrogen but still limited by other nutrients they are unable to utilise the increased nitrogen uptake, which accumulates resulting in detrimental effects such as increased stress, decomposition and competition from vascular species (Lamers *et al.* 2000, Limpens & Berendse 2003, Fritz *et al.* 2011).

Human use of fertilisers, fossil fuels and biological nitrogen fixation has more than tripled the amount of reactive nitrogen that is in circulation, from 31.6 Tg N yr<sup>-1</sup> in 1860 to 103 Tg N yr<sup>-1</sup> and it is predicted to rise to 195 Tg N yr<sup>-1</sup> by 2050 (Nitro Europe 2011, Galloway *et al.* 2004, Gu *et al.* 2010). Around 95 % of the increased NO<sub>x</sub> in the atmosphere is due to human activities, the remaining 5 % coming from natural processes such as forest fires, lightning and volcanoes (Pidwirny 2006). This

nitrogen can then follow a number of paths once released, via physical transportation, chemical transformations and surface deposition (Aneja *et al.* 2008). Increased reactive nitrogen in circulation can be involved in the formation of ozone, lung irritants and acid rain (Heeb *et al.* 2008, Petit & Bandosz 2008, Whitehead *et al.* 2008, Wood *et al.* 2008). An increase in the quantity of reactive nitrogen in the atmosphere will also result in an increase in the amount of nitrogen entering into nutrient poor ecosystems such as peatlands through wet and dry deposition (Gu *et al.* 2010), as it is estimated that approximately 70 % of emitted nitrogen is deposited over landmasses (Lamarque *et al.* 2005). As nitrogen is the primary limiting nutrient in ombrotrophic peatlands, an increase in available nitrogen would likely result in an increase in plant growth. It has been found that increased nitrogen deposition has been associated with a 10 – 26 % increase in carbon storage in forests and an increase in shoot extension and canopy height of *Calluna vulgaris* in peatlands (Nohrstedt *et al.* 1989, Carroll *et al.* 1999).

However, an increase of nitrogen into peatlands will not necessarily impact all vegetation species equally as some species will be capable of responding to increased nitrogen better than others, for example grasses may outcompete peatland dwarf shrubs (Prins *et al.* 1991, Bubier *et al.* 2007, Graglia *et al.* 2001). It is not yet known in what manner vegetation will respond to alterations in the available nitrogen and how it will affect the species composition within peatlands (Sheppard *et al.* 2004). It is suggested that low levels of nitrogen can increase growth of mosses such as *Sphagnum* spp and increase the nitrogen content (Nordbakken *et al.* 2003), however when large amounts of nutrients are available *Sphagnum* spp may not be as competitive as other species (Malmer *et al.* 2003). Evidence shows that nitrogen deposition can cause vascular plants to outcompete peatland mosses (Berendse *et al.* 2001, Bubier *et al.* 2007, Van Wijk *et al.* 2003) and potentially alter the carbon balance of the ecosystem and make ecosystems less stable during adverse conditions such as droughts (Bubier *et al.* 2007, Heijmans *et al.* 2001, Malmer & Wallén 2005, Galloway *et al.* 1995).

The impact of nitrogen deposition upon peatland ecosystems is not yet fully understood (Sheppard *et al.* 2004). As previously mentioned, numerous studies of

areas with nitrogen deposition have found varying effects of nitrogen deposition on vegetation and gaseous fluxes as have manipulative field experiments. As nitrogen deposition has been shown to have no impact in some studies, but alter vegetation communities and the carbon balance in others, additional work is needed to understand the processes involved.

## 3.2 Aims

This chapter covers a study at a long term experimental field site where doses of nitrogen have been added over a long term to peatland plots. It is hypothesised that increasing levels of nitrogen deposition will result in increased vegetation biomass and increased net ecosystem exchange (NEE). It is also hypothesised that higher doses of nitrogen will result in a greater proportion of vascular vegetation species within experimental plots. Field measurements were made of NEE and ecosystem respiration (ER) at the site to test this hypothesis by investigating whether the amount of nitrogen deposited on plots impacted on their CO<sub>2</sub> fluxes. Furthermore, the vegetation present was subjected to a survey and harvesting to investigate any treatment effect upon the vegetation community structure and the link between vegetation biomass and CO<sub>2</sub> exchange.

## 3.3 Methods

### 3.3.1 Site description

The study was carried out at a raised bog, Whim Moss, a field site established in 2002 by the UK Natural Environment Research Council's Global Nitrogen Atmospheric Enrichment (GANE) programme. A brief outline of the site and experimental setup is provided below and full details of the site can be found in Sheppard *et al.* (2004).

The site is located in the Scottish Borders, approximately 21 km south of Edinburgh at British National Grid reference NT203532. The site is 300 m above sea level and receives a mean annual rainfall of 900 mm. The depth of peat in the area ranges between 3 – 6 metres. The microtopography consists of hummocks and troughs ranging across the site, hummocks of moss and Sphagnum have been measured up to 35 cm in height. The main species at the site are *Calluna vulgaris*, *Erica tetralix*, *Eriophorum vaginatum*, *Sphagnum capillifolium*, *Sphagnum papillosum*, *Pleurozium schreberi*, *Polytrichum juniperinum*, *Hypnum jutlandicum* and *Cladonia portentosa*.

The site is adjacent to a horticultural peat extraction area but the experimental area has not been used for any peat extraction in the past and there is no management of vegetation through burning, mowing or grazing. The general area is grazed by rabbits and while the experimental site is fenced off to prevent access some grazing of the area by rabbits has been observed.



Figure 3.1. An aerial photograph of the field site. The rain collecting surface and building containing the data loggers and nitrogen concentrate containers can be seen on the right hand side. The deposition plots are positioned in between the boardwalks. Photograph: Ian Leith, CEH.

The experimental site covers approximately 0.5 ha and consists of 44 distinct plots with different treatments applied. There is a network of boardwalks that run alongside plots in order to minimise the impact of people walking around the site on the vegetation, hydrology and gas ebullition as seen in Fig. 3.1.

Of the 44 measurement plots shown in Fig. 3.2., only 28 plots were used due to constraints in time and available equipment. Four of the experimental plots were control plots and had no additional nitrogen deposited. The background deposition of nitrogen at the site is  $8 \text{ kg N ha}^{-1} \text{ y}^{-1}$ , so control plots were still subjected to some nitrogen deposition and therefore the total nitrogen deposition on the plots with nitrogen addition is  $8 \text{ kg N ha}^{-1} \text{ y}^{-1}$  higher than the dose amount indicated. The remaining 24 plots were subjected to six treatments depositing 8, 24 and  $56 \text{ kg N ha}^{-1} \text{ y}^{-1}$ , half as oxidised nitrogen,  $\text{NaNO}_3$ , and the other half as reduced nitrogen,  $\text{NH}_4\text{Cl}$ . The remaining 16 plots that were not used included doses of phosphorus and potassium in addition to nitrogen. The experimental site was divided into a four blocks which each had an identical number of different treatments applied to them in order to minimise any localised changes on the measurements.

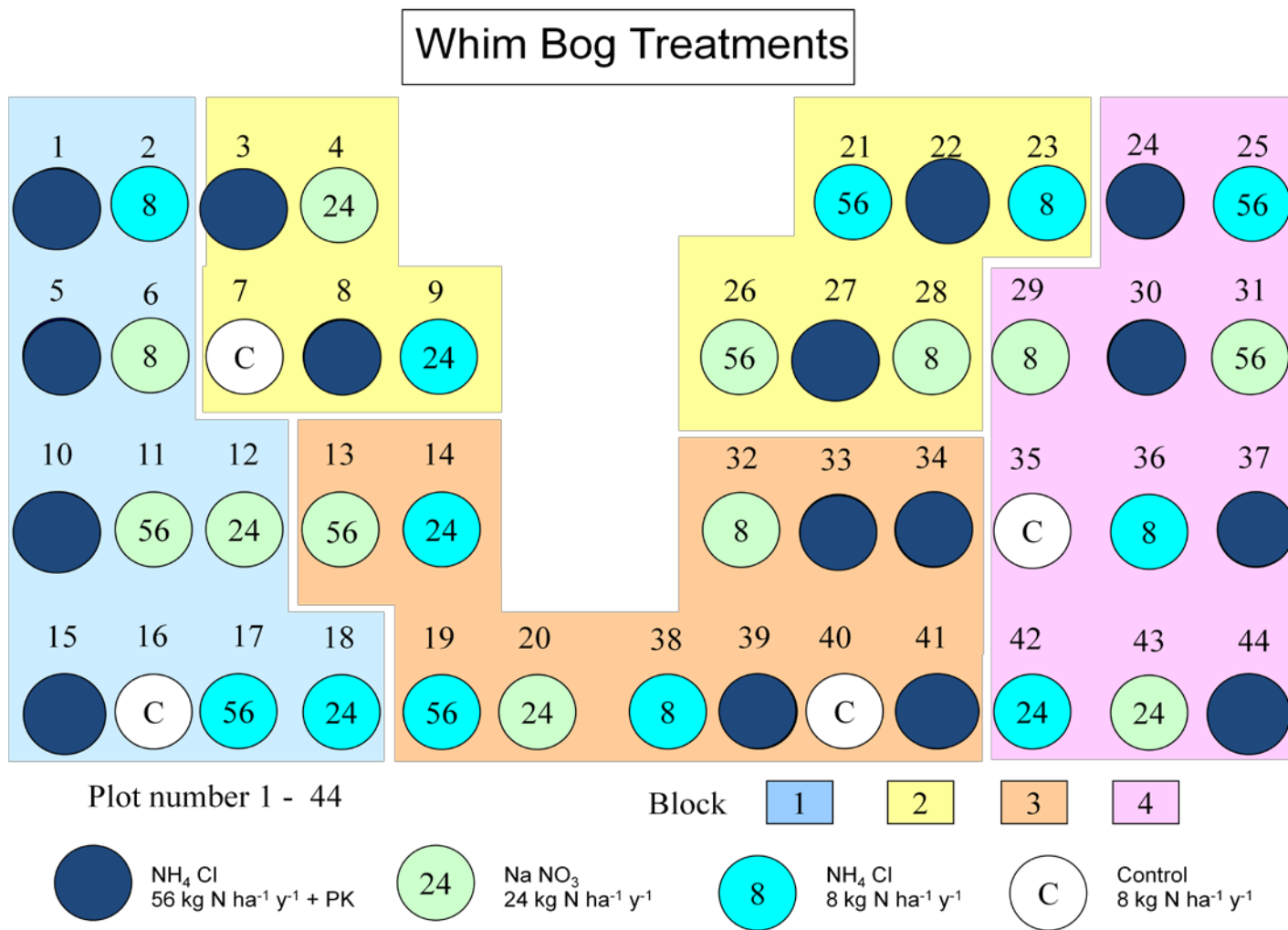


Figure 3.2. Diagram of Whim plot treatments. Plots with P and K additions are blanked out as they were not used in this study. The number within the plot circle indicates the level of the dose applied to that treatment and the colour indicates the form of nitrogen added. Source: Lucy Sheppard, CEH.

The site uses a 178 m<sup>2</sup> polythene covered surface to collect rain water in a 1250 L plastic tank and the water level in this tank is monitored by a float switch connected to a Campbell 23X data logger. The sprayers are only activated when there is sufficient water within the tank and when windspeed is <5 m s<sup>-1</sup> to prevent the treatment water being blown and deposited away from the experimental plot. Within the control shed a number of plastic containers were kept with the different treatment concentrations of N and P and K. The water from the rainfall tank is mixed with the solutions from these containers before being piped along 16 mm irrigation pipe to the plots where a sprayer head distributed it around the plot as seen in Fig. 3.3. Control plots were also sprayed with collected rainwater with no nutrient addition at the same time to ensure there were no differences in precipitation between control and treatment plots. The water delivered to the plots was equivalent to 3 mm hr<sup>-1</sup>. The delivery of treatment solutions to the plots was triggered by rainfall events measured by a tipping bucket rain gauge to ensure that the treatments were delivered at a realistic time that wet deposition would occur at the site. During periods where temperatures below 0 °C were expected the system would be operated manually to prevent sprayer heads being dislodged by frozen water and therefore not delivering treatments consistently on the plots. As the application of treatments was dependent on natural precipitation the times and length of spraying was irregular. Treatment application could take place a number of times during one day, or not at all based on natural precipitation. The quantity of liquid applied from the plastic containers was monitored to ensure that an equal amount of treatment solution was applied to each plot over the course of the year.



Figure 3.3 Treatment sprayer heads in the process of applying treatment water to plots. Source: Ian Leith.

### **3.3.2 Carbon dioxide measurements**

Measurements of NEE and ER were made using the method described in Chapter 2. Each of the 24 plots being measured had a chamber base randomly inserted that was left in-situ in between measurements. There were up to five CO<sub>2</sub> analysers available for use, although all five analysers were not always able to be used due to equipment malfunctions. A single analyser was used to measure ER using the modified darkened chamber and the remaining analysers available, up to four, measured NEE using a transparent chamber.

Measurements were typically carried out over a 48 hour period starting early in the morning of the first day and continuing until the evening in order to obtain a significant number of flux measurements for a range of environmental conditions in order to model the flux responses to PAR, temperature and hydrology. At the start of measurements all analysers were spread across the experimental plots and commenced measurements. The analysers were set to average a flux measurement over a two minute period and were set on an individual plot for between 15 – 20 minutes. After this period all of the analysers were moved to their next measurement plot. This continued for the duration of the measurement period and ensured that each plot was measured at least once by each individual CO<sub>2</sub> analyser and that there were a range of measurements throughout the day for each plot. Measurements for individual plots were compared between analysers to identify whether an analyser had malfunctioned during the measurement period so that measurements made by it could be excluded. Measurements were carried out on four separate occasions between September 2010 – June 2011.

For the period that measurements were made a CR10X datalogger (Campbell Scientific) was used to record average environmental variables at 1 minute intervals. The datalogger was synchronised to the internal clocks on the CO<sub>2</sub> analysers prior to the start of the measurement period to permit the environmental data on the datalogger to be matched up to measurements from the CO<sub>2</sub> analysers. Air temperature was monitored using a 107 thermistor probe located within a radiation shield (Campbell Scientific) and PAR was monitored using a PAR Quantum sensor (Skye Instruments). These sensors were located in the centre of the experimental area and positioned approximately 1 metre above the ground. In addition each CO<sub>2</sub> analyser had a CR200 datalogger (Campbell Scientific) attached to it with a 109 thermistor probe (Campbell Scientific) which was used to record the soil temperature at individual plots.

### 3.3.3 Vegetation survey and harvesting

To determine whether nitrogen deposition was having any impact upon the vegetation within the experimental plots, a vegetation survey and harvesting of vegetation within the plots used for flux measurements was carried out after the final set of CO<sub>2</sub> measurements had been completed.

A survey was carried out on the vegetation present inside each chamber base to produce an estimate of the quantity of each species present. The percentage of the plot surface area covered by each species was estimated by a visual observation. Species with significant vertical height had their length measured several times in different areas to give a representative mean height of the vegetation within the plot. Species with woody stems had their total length and the length of their green shoots measured. For mosses and *Sphagnum* the area of ground covered within the plot was calculated based on the estimated percentage cover recorded and the area inside the chamber base. The height of the top of the mosses above the soil was also measured.

Once the final gas flux measurements had been completed at the site, in October 2011 all of the plots had their vegetation harvested so the exact biomass of the individual species present could be measured. Vegetation was removed down to the soil surface and sorted by species. Vegetation with woody stems was separated into the wood and green components. The sorted vegetation was placed in paper bags and inside an oven set at 70°C for a minimum of 48 hours to remove moisture from the vegetation, after which it was weighed.

Prior to being placed in the oven, the harvested moss and *Sphagnum* vegetation was laid out on a work surface and the surface area that it covered was measured. For several harvested plots, the *Eriophorum* and *Calluna* green shoots were examined on a LI-3100 leaf area meter (Li-Cor Environmental) to determine the leaf area index of those plots. This was then used to produce a calibration curve for leaf area index

based on the vegetation mass harvested from the plots. This calculation was then used to estimate the leaf area index for the remaining plots based on the harvested vegetation mass.

### **3.3.4 Data analysis and statistics**

Analytical software packages Minitab 16 (Minitab Inc.) and GenStat 14 (VSN International) were used to perform analysis of the data. As measurements of NEE and ER did not take place simultaneously across all plots, the measured fluxes were related to recorded environmental measurements at the site in order to determine the flux response of the plot.

NEE measurements were related to PAR using the equation  $NEE = A + B \times (R^{PAR})$ , developed within GenStat to model vegetation responses to solar radiation. ER was related to water table depth using a linear regression  $ER = A + B \times WT$ . The constants derived from these relationships and the flux values calculated by these relationships were tested with a T-Test and ANOVA to determine if there were differences between the treatments.

## 3.4 Results

### 3.4.1 NEE measurements

NEE flux measurements ranged between  $-11.00$  to  $2.79 \mu\text{mol m}^{-2} \text{s}^{-1}$  during the analysis period. There was no difference between oxidised and reduced forms of nitrogen, therefore both forms were analysed together. The mean flux of the control plots was  $-2.02 \mu\text{mol m}^{-2} \text{s}^{-1}$ , while the mean flux of the  $8 \text{ kg N ha}^{-1} \text{y}^{-1}$  treatment plots was significantly different at  $-2.61 \mu\text{mol m}^{-2} \text{s}^{-1}$  (T-test,  $P < 0.001$ ) and the mean flux of the  $24 \text{ kg N ha}^{-1} \text{y}^{-1}$  was significantly lower,  $-1.74 \mu\text{mol m}^{-2} \text{s}^{-1}$  (T-test  $P = 0.005$ ), while the  $56 \text{ kg N ha}^{-1} \text{y}^{-1}$  treatment was not significantly different to the control plots, as seen in Fig. 3.4, the  $56 \text{ kg N ha}^{-1} \text{y}^{-1}$  mean being  $-2.04 \mu\text{mol m}^{-2} \text{s}^{-1}$ , (T-test  $P = 0.822$ ). Although the  $8 \text{ kg N ha}^{-1} \text{y}^{-1}$  treatment had significantly greater  $\text{CO}_2$  uptake than the control plots, the  $24 \text{ kg N ha}^{-1} \text{y}^{-1}$  treatment had lower uptake and  $56 \text{ kg N ha}^{-1} \text{y}^{-1}$  treatment was not significantly different to the control, therefore this significant difference may not be due to the nitrogen addition treatment effect.

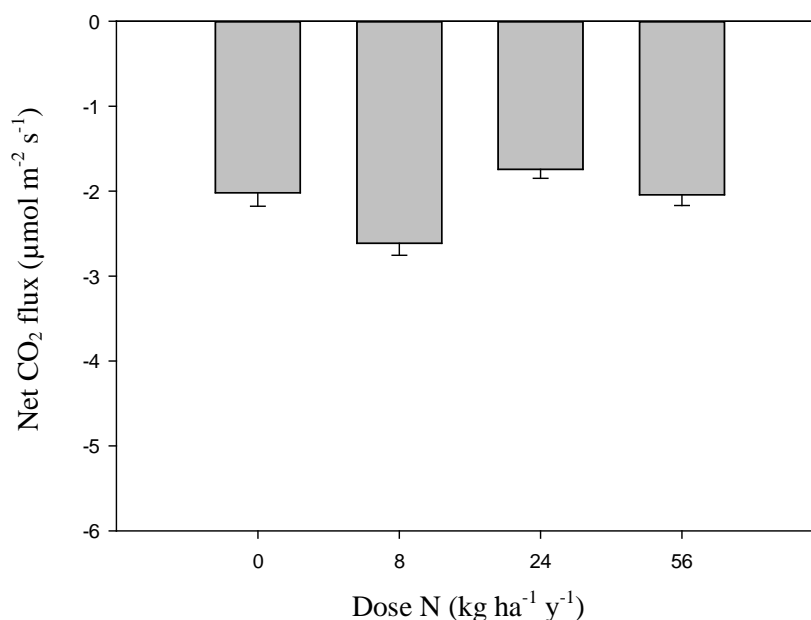


Figure 3.4. A bar graph showing the mean NEE measurements for each treatment dose. Error bars indicate 95 % confidence intervals.

Due to fluxes at the site being measured over an extended period of time under different environmental conditions, the fluxes were modelled against environmental variables in order to compare the plots without the variance of environmental conditions. PAR was the most significant environmental variable for explaining variations in NEE fluxes, therefore the individual fluxes for each plot were plotted against the corresponding measurement of PAR to allow the comparison between plots. The light response of each plot was modelled by using the relationship  $\text{Flux} = A + B \times (R^{\text{PAR}})$ . The constant components of the curve were analysed for treatment effects, however there were no significant differences, R ( $F = 0.94$ ,  $P = 0.438$ ), B ( $F = 0.19$ ,  $P = 0.903$ ) and A ( $F = 0.21$ ,  $P = 0.889$ ).

The light response curves were used to calculate modelled fluxes for each plot at specific levels of PAR to examine treatment effects on flux values, a range of which are seen in Table 3.1. The maximum PAR recorded during the measurement periods was  $1520 \mu\text{mol s}^{-1} \text{m}^{-2}$ . The mean modelled fluxes at  $1500 \mu\text{mol s}^{-1} \text{m}^{-2}$  ranged from  $-3.96$  to  $-5.59 \mu\text{mol m}^{-2} \text{s}^{-1}$ .

Table 3.1. Mean modelled NEE fluxes ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) for selected levels of PAR up to  $1500 \mu\text{mol s}^{-1} \text{m}^{-2}$ . A one way ANOVA was used to investigate any treatment effect between doses.

PAR ( $\mu\text{mol s}^{-1} \text{m}^{-2}$ )	Dose N ( $\text{kg ha}^{-1} \text{y}^{-1}$ )				F value	P value
	0	8	24	56		
300	-1.58	-2.44	-1.65	-1.76	2.85	0.059
600	-2.95	-3.94	-2.66	-3.10	2.61	0.074
900	-3.90	-4.77	-3.28	-3.95	2.10	0.126
1200	-4.56	-5.27	-3.68	-4.52	1.66	0.201
1500	-5.03	-5.59	-3.96	-4.91	1.34	0.284

The modelled NEE measurements showed no significant treatment effect at any level of PAR as seen in Fig. 3.5. At lower levels of PAR there was almost a significant difference between plots treated with  $8 \text{ kg N ha}^{-1} \text{y}^{-1}$  and the control and other

treatment plots ( $F = 2.85$ ,  $P = 0.059$ ). The plots at this treatment level had the highest  $\text{CO}_2$  uptake, however there was no correlation between the fluxes and the dose ( $P = 0.225$ ), as with the raw flux measurements. The plots receiving the  $8 \text{ kg N ha}^{-1} \text{ y}^{-1}$  had the highest NEE fluxes at all the levels of PAR, however at higher levels of modelled PAR the difference in fluxes between treatments decreased.

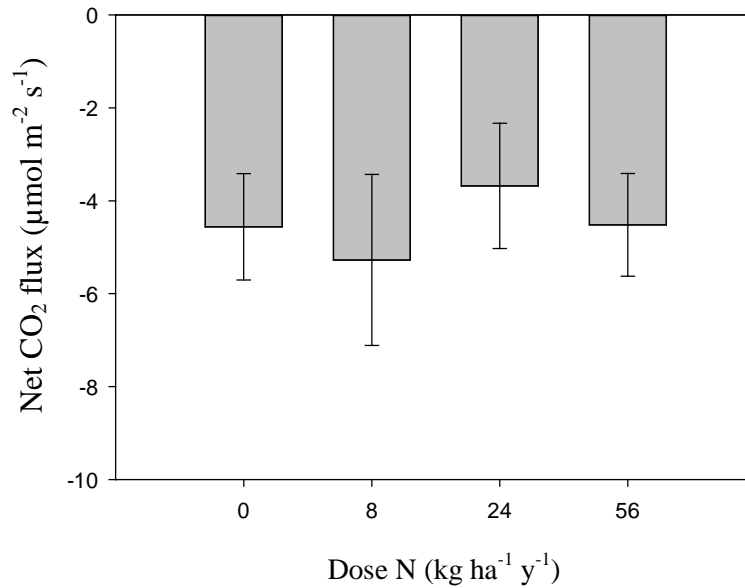


Figure 3.5. Bar graph of mean modelled NEE by dose at a PAR level of  $1200 \mu\text{mol s}^{-1} \text{ m}^{-2}$ . A negative flux indicates an uptake of  $\text{CO}_2$  by the vegetation. Error bars represent 95 % confidence intervals.

### 3.4.2 Ecosystem Respiration

ER measurements ranged from 0.01 – 2.79  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , the mean flux of the control plots being 0.39  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . As shown in Fig. 3.6. the fluxes from the control plots were significantly different to the 8 kg N  $\text{ha}^{-1} \text{y}^{-1}$  dose (T-test,  $P = 0.017$ ), which had a mean flux of 0.56  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . The 24 and 56 kg N  $\text{ha}^{-1} \text{y}^{-1}$  treatments were not significant (T-test,  $P = 0.351$  and  $P = 0.088$  respectively) with mean fluxes of 0.33  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and 0.52  $\mu\text{mol m}^{-2} \text{s}^{-1}$  respectively.

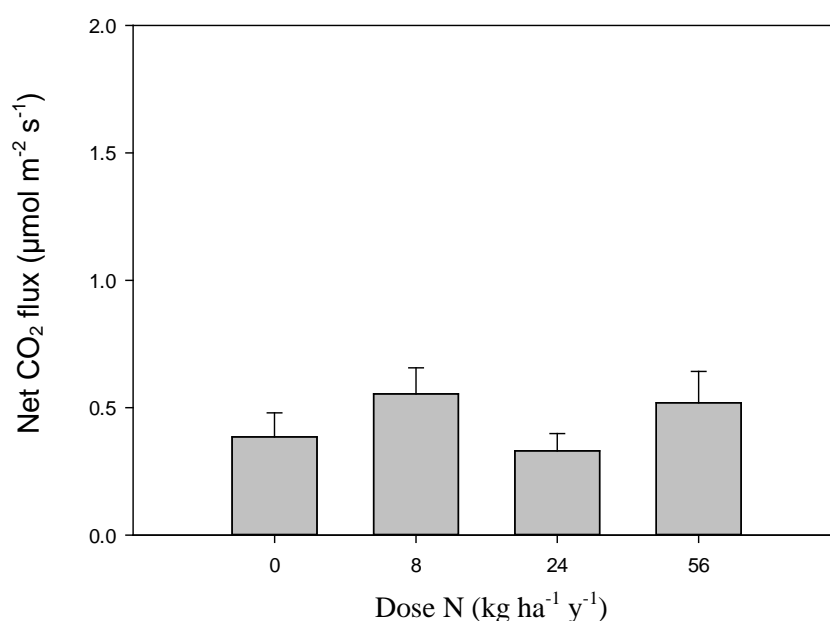


Figure 3.6. A bar graph showing the mean CO<sub>2</sub> respiration for each treatment dose. Error bars indicate 95 % confidence intervals.

As with the NEE measurements, ER measurements were made over a range of times, therefore the fluxes measured at the site were modelled against the water table depth to account for changes in environmental conditions. A linear regression for each plot was made to allow for comparisons between plots as seen in Fig. 3.7. The constant parameters defining the lines were examined for treatment differences, however none were significant, constant ( $F = 0.58$ ,  $P = 0.632$ ), water table multiplier ( $F = 1.54$ ,  $P = 0.229$ ).

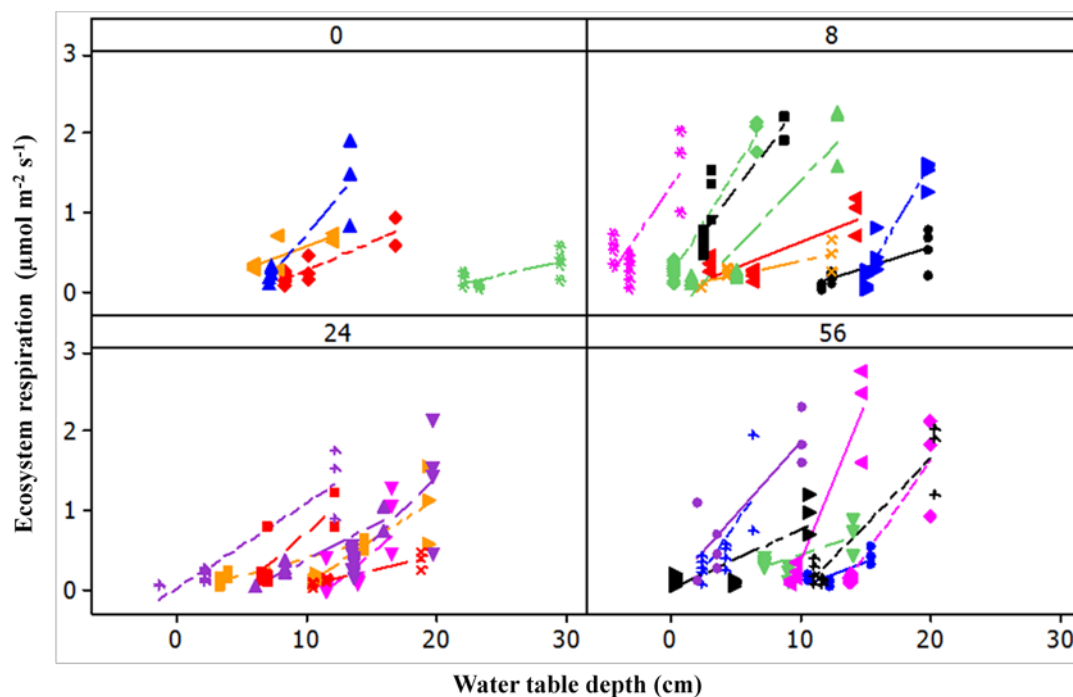


Figure 3.7. Ecosystem respiration plotted against water table depth with linear regressions fitted. Separate panels indicate the different doses of N ( $\text{kg ha}^{-1} \text{y}^{-1}$ ) applied to the experimental plot as indicated by the panel heading. The different symbols within the graph each refer to an individual measurement plot.

As with NEE measurements, the fitted lines for each plot were used to predict the fluxes for a specific water table level. There were no significant differences in  $\text{CO}_2$  respiration for different treatments as shown in Table 3.2 and Fig. 3.8. Additionally there was no correlation between the plot respiration and the dosage ( $P \geq 0.177$ ), suggesting that there was no treatment effect on ER.

Table 3.2. Mean modelled CO<sub>2</sub> respiration fluxes by dose at a range of water table depths. Differences between the treatments were examined with a one way ANOVA.

Water table depth (cm)	Dose N (kg ha <sup>-1</sup> y <sup>-1</sup> )				F value	P value
	0	8	24	56		
0	-0.57	-0.37	-0.74	-1.17	0.58	0.632
5	-0.12	0.47	-0.22	-0.27	0.82	0.494
10	0.33	1.31	0.30	0.62	1.41	0.265
20	1.22	2.98	1.34	2.41	2.02	0.138

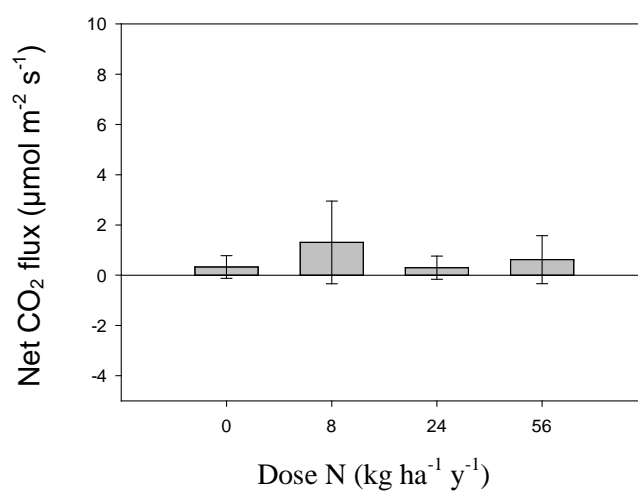


Figure 3.8. Predicted ER measurements at water table depth of 10 cm, based upon linear regressions applied to field measurements shown in Fig. 3.7.

### 3.4.3 Vegetation survey and harvesting

As seen in Table 3.3 the majority of the harvested vegetation mass was due to *Calluna vulgaris* and non-*Sphagnum* moss species, which accounted for 44.5 % and 38.2 % of the total vegetation mass respectively. *Eriophorum* and *Sphagnum* accounted for 6.3 % and 7.8 % of the total vegetation mass harvested. *Calluna* and *Eriophorum* vegetation were the only species that were present in every plot. The ground cover varied between moss and *Sphagnum* species. 21 of the plots only had moss species present, 2 had only *Sphagnum* species and 5 had both moss and *Sphagnum* present.

Table 3.3. Mean vegetation mass per area ( $\text{g m}^{-2}$ ) by dose for the treatment levels. Data were analysed using a one way ANOVA for differences between treatments.

Variable	Dose N ( $\text{kg ha}^{-1} \text{y}^{-1}$ )				F value	P value
	0	8	24	56		
<i>Calluna</i> Total	730	1178	860	1111	0.93	0.441
<i>Calluna</i> woody	430	584	504	609	0.31	0.818
<i>Calluna</i> Green shoots	300	594	357	502	2.37	0.095
<i>Eriophorum</i>	210	168	63	159	2.34	0.099
Moss & <i>Sphagnum</i>	1159	1210	1087	1018	0.33	0.801
All vegetation	2100	2555	2010	2288	1.08	0.338

As shown in Fig. 3.9. there was no observed treatment effect on the total mass of vegetation (ANOVA,  $P = 0.338$ ). There were also no significant treatment differences in the mass of any individual vegetation species measured at the site as shown in Table 3.3, although *Eriophorum* and *Calluna* green shoots were nearly significant. There was also no correlation between vegetation mass and the dose applied to the plot for any of the species present, all vegetation ( $P = 0.835$ ), total *Calluna* ( $P = 0.607$ ), green *Calluna* ( $P = 0.740$ ), *Eriophorum* ( $P = 0.664$ ) and moss & *Sphagnum* ( $P = 0.350$ ).

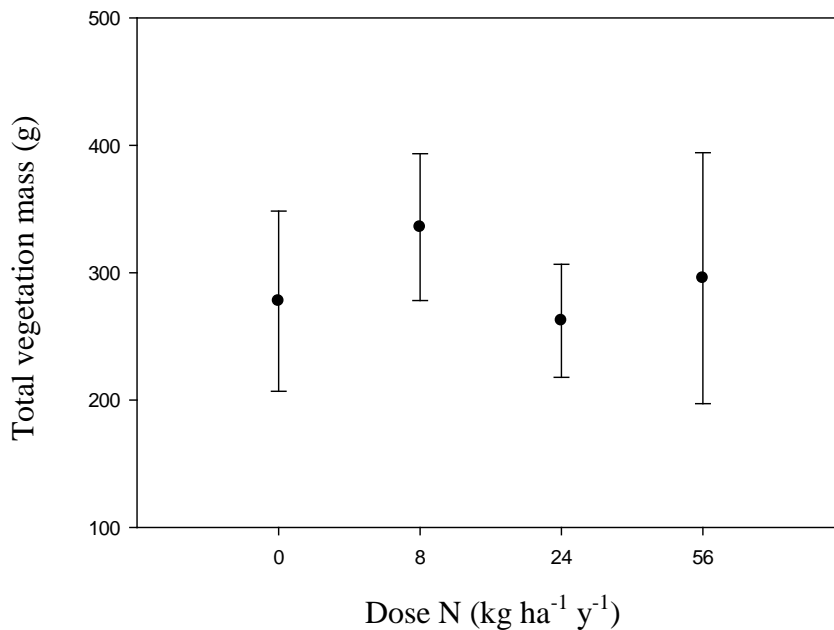


Figure 3.9. A scatterplot showing the mean plot vegetation mass by treatment dose. Error bars show 95 % confidence intervals.

### 3.4.4 Estimating biomass from vegetation survey

The most accurate method to determine the biomass present in a particular area requires the harvesting of vegetation and the separation, drying and weighing of individual species. However, this prevents any further study of the area due to the removal of the vegetation. It is therefore desirable to be able to calculate the biomass within an area by non destructive means. A multivariate regression was used to analyse the relationship between the vegetation mass harvested and the percentage ground cover and vegetation length recorded from the pre harvest vegetation survey shown in Appendix A. This was applied to the total vegetation and green portions of *Calluna vulgaris* and *Eriophorum vaginatum* as they were the dominant species with significant shoot length within the plots. From these regressions, the equations below were derived for use to estimate the biomass present based on non destructive vegetation surveying, where  $M$  is vegetation dried mass ( $\text{g m}^{-2}$ ),  $C$  is vegetation

percentage ground cover and L is vegetation length (cm). These relationships are illustrated in Fig. 3.10.

$$M_{Calluna} = -241 + 12.1 \times C + 11.7 \times L_{TOTAL} \quad (3.1)$$

$$(R^2 = 0.70, P < 0.001)$$

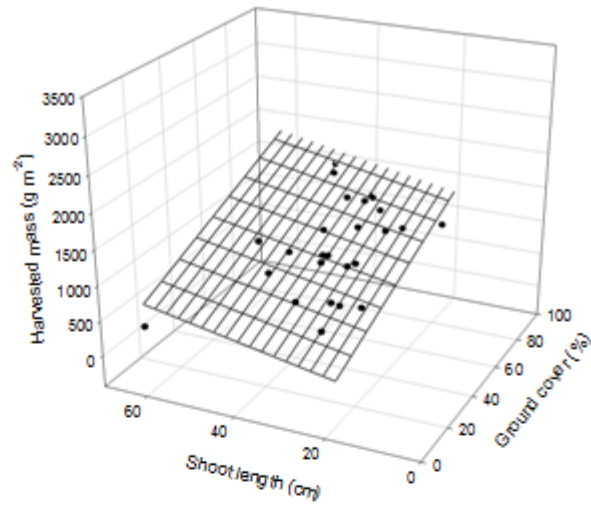
$$M_{Green\ Calluna} = 114 + 6.19 \times C - 5.97 \times L_{GREEN} \quad (3.2)$$

$$(R^2 = 0.74, P < 0.001)$$

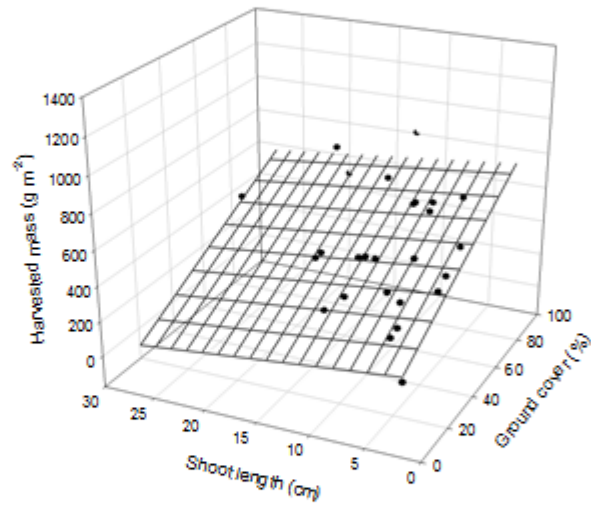
$$M_{Eriophorum} = 57 + 3.47 \times C - 0.29 \times L \quad (3.3)$$

$$(R^2 = 0.83, P < 0.001)$$

A



B



C

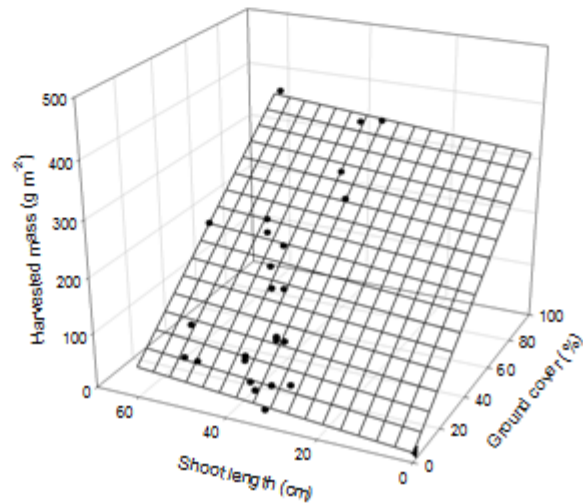


Figure 3.10. 3D scatter graphs showing the relationship between ground cover, shoot length and the weighed mass of harvested vegetation that the multivariate regressions were based on. Graph A shows the relationship for total *Calluna vulgaris*, Graph B shows the relationship for the green shoots of *Calluna vulgaris* and Graph C shows the relationship for *Eriophorum vaginatum*.

Estimating the mass of mosses and *Sphagnum* species from the vegetation survey was more challenging than for vascular plants. There was no correlation between the harvested measured mass and the estimated area from the vegetation survey as seen in Fig. 3.11. ( $r = 0.150$ ,  $P = 0.447$ ) or depth ( $r = 0.103$ ,  $P = 0.601$ ). The data were complicated as the vegetation survey indicated that 16 of the 28 plots were judged to have 100 % ground cover of either moss or *Sphagnum*, but no indication of density could be derived. As seen in Fig. 3.11. this resulted in a clustering of points at the plot surface area of 1256.64 cm<sup>2</sup>. In addition, due to the nature in which dead *Sphagnum* and moss decay within peatlands it was not straightforward determining where the vegetation ended and the soil began. As a result, variations in mass may be due in part to inconsistencies in the depth of vegetation that was harvested, due to variations in levels of decomposition.

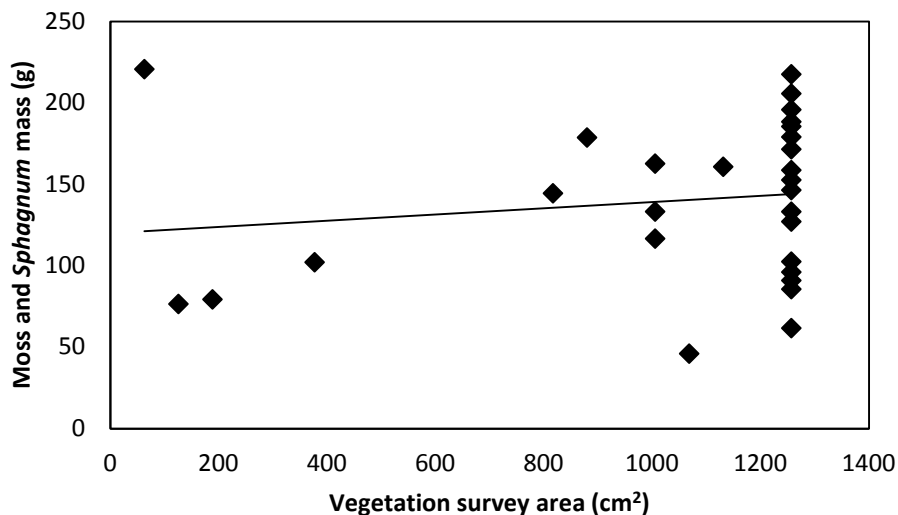


Figure 3.11. The weighed moss and *Sphagnum* mass plotted against the area estimated from the vegetation survey.

Prior to being put in the oven for drying, the moss and *Sphagnum* samples were laid out on a workbench and the surface area they covered was measured, hereafter referred to as the laboratory measured area for the species. This was found to correlate with the dried mass ( $r = 0.462$ ,  $P = 0.013$ ) as seen in Fig. 3.12. This provided a method of estimating the mass of the mosses from the laboratory measured area of moss and *Sphagnum* from the plots without having to dry and weigh them. However, obtaining the laboratory measured area still required the moss

and *Sphagnum* to be harvested from the plots in order to measure the surface area covered.

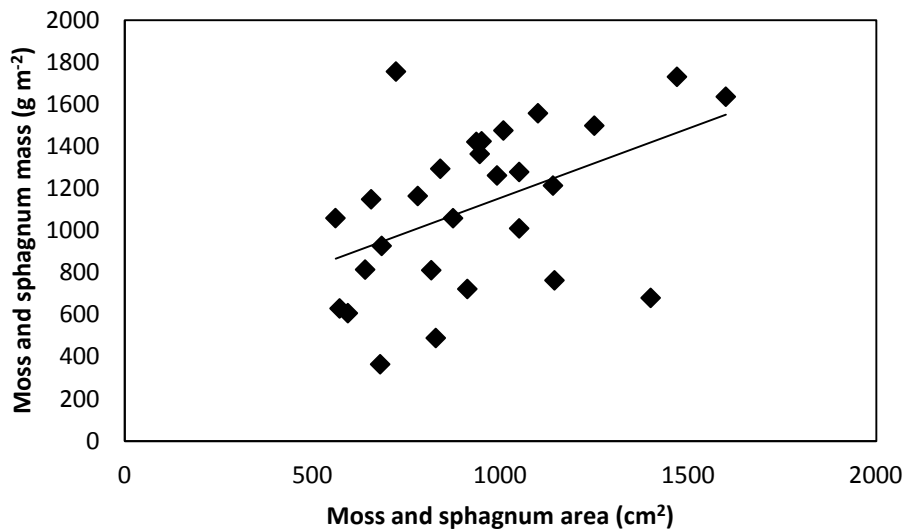


Figure 3.12. The weighed moss and Sphagnum mass plotted against the ground area covered, measured prior the vegetation being placed in the oven.

It was found that the laboratory measured area correlated with the surface area determined from the vegetation survey ( $r = 0.534$ ,  $P = 0.003$ ). This provided a link to determine the laboratory measured area from the vegetation survey and subsequently the vegetation mass from the laboratory measured area. However, as seen in Fig. 3.13. this relationship was still skewed by the number of plots that were given a percentage cover of 100 % and 1256.64 cm<sup>2</sup> during the vegetation survey.

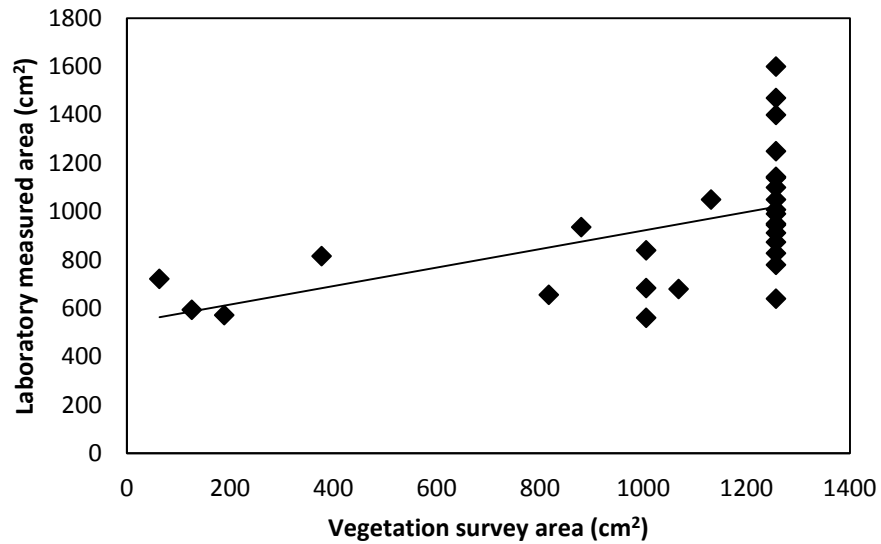


Figure 3.13. The moss and *Sphagnum* measured area plotted against the area calculated from the vegetation survey.

From the relationships shown in Figs. 3.12 and 3.13 equations 3.4 and 3.5 were derived using a linear regression in order to determine the laboratory measured area of moss and *Sphagnum* from the vegetation survey and subsequently the vegetation mass from the laboratory measured area.

$$A_{\text{LABORATORY MEASURED}} (\text{cm}^2) = 538 + 0.383 \times A_{\text{VEGETATION SURVEY}} (\text{cm}^2) \quad (3.4)$$

$$(R^2 = 0.29, P = 0.003)$$

$$M = 497 + 0.658 \times A_{\text{LABORATORY MEASURED}} \quad (3.5)$$

$$(R^2 = 0.21, P = 0.013)$$

Where A is the surface area ( $\text{cm}^2$ ), either from the vegetation survey of laboratory measured area and M is the vegetation mass ( $\text{g m}^{-2}$ ).

### 3.4.5 Determining LAI from mass

The *Calluna vulgaris* green shoots and *Eriophorum vaginatum* leaves from a number of plots had their leaf area measured to determine their leaf area index (LAI). These plots were used to develop a calibration curve to estimate the LAI from the vegetation mass. As seen in Fig. 3.14, the measured LAI for *Calluna vulgaris* and *Eriophorum vaginatum* correlated with the harvested mass and a linear regression could therefore be used to estimate the LAI based on vegetation mass.

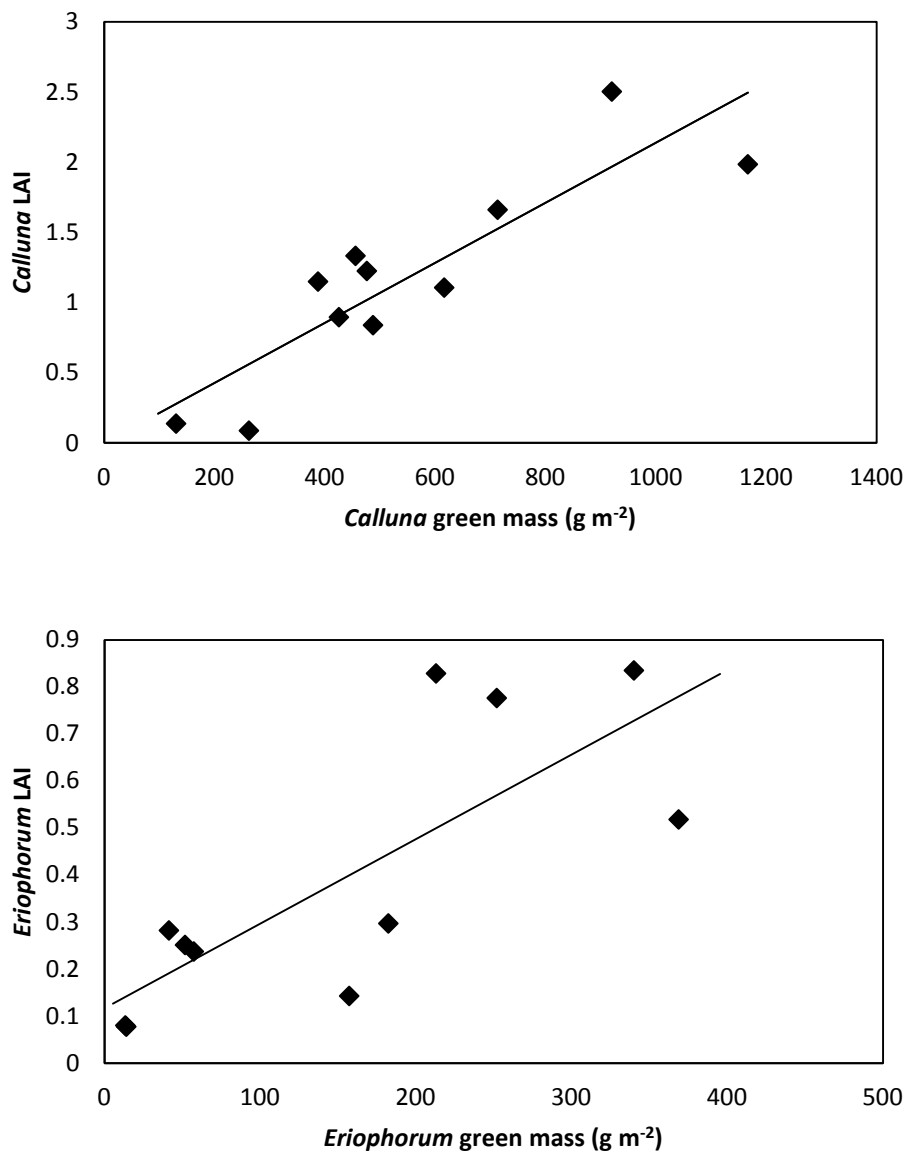


Figure 3.14. The measured leaf area index for Green *Calluna* shoots and *Eriophorum* plotted against vegetation harvested mass m<sup>-2</sup>.

A linear regression was used to determine the equations that could be used to estimate the LAI based on the vegetation mass:

***Calluna* LAI calculated from mass:**

$$\text{LAI} = 0.0021 \times M - 0.0003 \quad (3.6)$$

$$(R^2 = 0.77, P < 0.001)$$

***Eriophorum* LAI calculated from mass:**

$$\text{LAI} = 0.0018 \times M + 0.1169 \quad (3.7)$$

$$(R^2 = 0.62, P = 0.004)$$

Where LAI is the leaf area index and M is the vegetation mass ( $\text{g m}^{-2}$ ).

To determine the LAI of moss and *Sphagnum*, the laboratory measured area was assessed to be the most accurate indication of moss and *Sphagnum* area. This was divided by the plot ground surface area to give the LAI.

The relationship between leaf area index of all the vegetation species surveyed and exchange of  $\text{CO}_2$  was investigated. The NEE flux correlates strongly with the LAI ( $r = -0.818, P < 0.001$ ) as seen in Fig.3.15. The ER flux also correlates with the LAI ( $r = 0.534, P = 0.003$ ), however it does not take into account as much of the variation as for NEE as shown in Fig. 3.16, possibly as the LAI does not take into account variations in the ER between plots from sources other than vegetation.

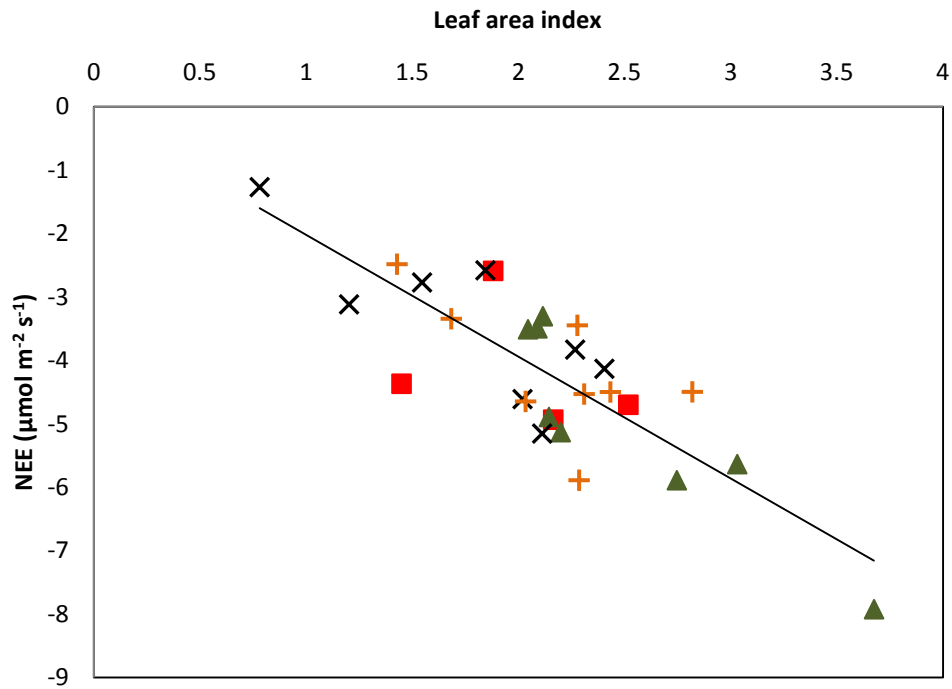


Figure 3.15. The modelled NEE for all plots at a PAR level of  $1000 \mu\text{mol s}^{-1} \text{m}^{-2}$  plotted against the calculated leaf area index. The different symbols indicate the various dose levels:  $\blacksquare$  0,  $\blacktriangle$  8,  $\times$  24,  $+$  56  $\text{kg N ha}^{-1} \text{y}^{-1}$ .

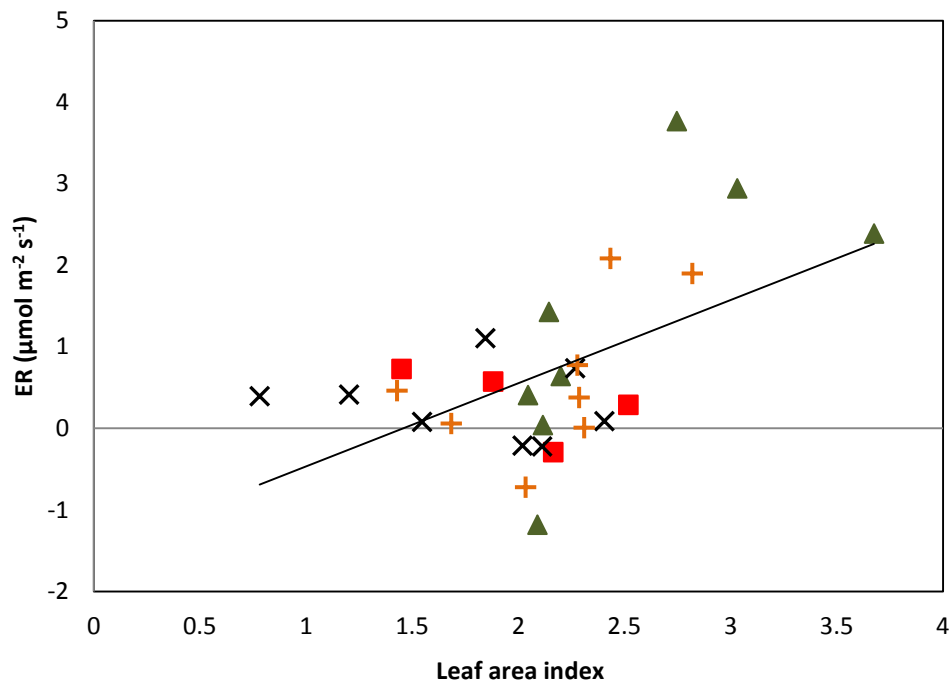


Figure 3.16. Ecosystem respiration at 10 cm water table depth plotted against the calculated leaf area index. The different symbols indicate the dose levels:  $\blacksquare$  0,  $\blacktriangle$  8,  $\times$  24,  $+$  56  $\text{kg N ha}^{-1} \text{y}^{-1}$ .

From the relationships shown in Figs. 3.15 and 3.16 equations 3.8 and 3.9 were derived using a linear regression. This allowed the NEE and ER to be predicted for the site at a specified level of PAR or water table depth respectively without the need for a CO<sub>2</sub> analyser to be used.

#### **Calculation of NEE from LAI**

$$NEE_{PAR\ 1000} = -1.92 \times LAI - 0.101 \quad (3.8)$$

$$(R^2 = 0.67, P < 0.001)$$

#### **Calculation of ER from LAI**

$$ER_{WT\ -10} = 1.02 \times LAI - 1.49 \quad (3.9)$$

$$(R^2 = 0.29, P = 0.003)$$

Where NEE is net ecosystem exchange at the specified level of PAR ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ), ER is ecosystem respiration at the specified water table depth (cm) and LAI is the leaf area index.

It should be possible from equation 3.8 to estimate the soil respiration value of a plot by inputting the LAI value to zero. However, this gives a value of  $-0.101 \mu\text{mol m}^{-2} \text{s}^{-1}$  for soil respiration, which cannot be an accurate figure as it indicates an uptake of CO<sub>2</sub> even with no vegetation present.

### 3.5 Discussion

It has been suggested that as nitrogen is a limiting factor in plant growth, adding nitrogen to an ecosystem should allow increased plant growth (Gruber & Galloway 2008). As ombrotrophic bogs are typically nutrient poor, it was expected that an increase in available nitrogen would cause an increase in vegetation growth and the amount of CO<sub>2</sub> uptake. However, in spite of the large amounts of nitrogen being added to the plots on the site there was no detectable difference in the vegetation within the plots or the carbon exchange between treatments. While this was unexpected, a similar limited impact of nitrogen deposition has been observed in similar studies (Bubier *et al.* 2007, Saarnio *et al.* 2003).

#### Changes to vegetation growth

In principle an increase in nitrogen availability was expected to result in an increase in vegetation growth and total biomass (Rydin & Jeglum 2006, Walker & Steffen 1997). It was therefore unexpected to see no treatment effects on the total vegetation mass or on the vegetation mass of individual species. Studies such as Van Wijk *et al.* (2003), Berendse *et al.* (2001) and Malmer *et al.* (2003) indicated that an increase in nitrogen may result in a shift in vegetation species away from mosses towards vascular plants, however there was no indication of a treatment effect upon species composition from vegetation surveying or harvesting. A meta-analysis found that high levels of nitrogen reduced the productivity of *Sphagnum* mosses (Limpens *et al.* 2011). Limpens *et al.* (2008) indicated that nitrogen deposition of above 10 - 15 kg ha<sup>-1</sup> y<sup>-1</sup> would be sufficient to increase the cover of vascular plants and decrease *Sphagnum* moss cover, although they did add that changes may take a significant amount of time to take place and difficult to identify experimentally. There was no evidence of this the site, however only a third of the plots contained *Sphagnum* species, therefore such an effect may not have been detectable on the limited number of plots.

In addition to having low levels of nitrogen, peatlands have low levels of other nutrients needed by plants, such as potassium and phosphorus, and therefore even if

nitrogen is increased to a high level, the vegetation may not be able to utilise it due to a lack of these other nutrients. While Juutinen *et al.* (2010) and Saarnio *et al.* (2003) found there was no impact of adding nitrogen by itself, if phosphorus and potassium were added to plots as well as nitrogen there was a change in vegetation community structure and an increase in the ecosystem respiration. Bragazza *et al.* (2012) found that phosphorus became the limiting nutrient in microbe decomposition once high levels of nitrogen were applied, therefore a vegetation and microbial shift may not have been observed in the experimental plots as the vegetation was still limited by phosphorus.

In a similar experimental study, Fritz *et al.* (2012) found that deposition of 40 kg N ha<sup>-1</sup> y<sup>-1</sup> was sufficient to double the concentrations of nitrogen within *Sphagnum* tissues to 14.5 mg N g<sup>-1</sup> DW and indicate the vegetation was stressed. An increased level of nitrogen can have toxic effects for vegetation, if for example it cannot be used for increased growth due to further nutrient limits on growth (Nordin & Gunnarsson 2000, Van der Wal *et al.* 2005). As the high N doses in this study exceed 40 kg N ha<sup>-1</sup> y<sup>-1</sup>, the vegetation within these plots may have been stressed and unable to increase growth due to a lack of other nutrients.

### **Net Ecosystem Exchange and Ecosystem Respiration**

The most significant part of CO<sub>2</sub> exchange is due to vegetation and prior to the start of measurements it was hypothesised that CO<sub>2</sub> uptake would increase as the level of nitrogen deposition was increased. However, as measurements of biomass did not show any treatment effect it was therefore not surprising that there was not a treatment effect detected by NEE measurements either. In similar studies no increase in CO<sub>2</sub> uptake was observed with an increase in nitrogen and a decrease in CO<sub>2</sub> observed at high levels of nitrogen deposition (Bubier *et al.* 2007, Saarnio *et al.* 2003). Bragazza *et al.* (2012) reported that an increase in nitrogen led to the decomposition rate increasing and therefore a reduction in the carbon accumulation. A similar long term nitrogen deposition study in northern Canada found a similar result that nitrogen deposition by itself does not significantly change the flux

(Juutinen *et al.* 2010). In Bubier *et al.* (2007) nitrogen treatments resulted in a significant increase in the peat bulk density, which could indicate that there has been higher peat decomposition or a loss of *Sphagnum* moss, however in this study there was no significant impact of treatment upon vegetation or ER identified. Both of these changes would have the potential to alter the CO<sub>2</sub> balance through a change in the decomposition rate, oxygen availability and water transportation. Although there were not significant changes observed due to the treatments, it was noted that the 8 kg N ha<sup>-1</sup> y<sup>-1</sup> treatment had the highest NEE uptake and ER. It has been observed that a low level of nitrogen addition can increase the amount of *Sphagnum* growth (Nordbakken *et al.* 2003), it is therefore possible a low dose might stimulate increased vegetation growth and photosynthesis, while higher doses can stress vegetation and increase decomposition leading to a loss of CO<sub>2</sub> (Fritz *et al.* 2012).

A possible reason for a lack of observed treatment effects stems from the fact that this peatland site is subjected to background atmospheric nitrogen deposition of 8 kg N ha<sup>-1</sup> y<sup>-1</sup>. While the control plots did not receive any additional nitrogen input from the experimental setup, they already had a significant amount of nitrogen added from background deposition. The critical load, the level of pollution at which the ecosystem is significantly impacted, for raised and blanket bogs has been estimated to be 5 -10 kg ha<sup>-1</sup> y<sup>-1</sup> (UNECE 2010). As the background deposition rate at Whim Moss is already within that range, it is possible that even the control plots have already responded to the background level of nitrogen and any further change is being limited by other factors, for example a lack of additional nutrients such as phosphorus and sulphur. Once the ecosystem has reached a level of nitrogen saturation, the addition of further nitrogen will have no impact on plant growth and may leach out of the ecosystem (Vitousek *et al.* 1997). If the experimental site has reached a level of nitrogen saturation through background deposition, then the experimental depositing of further nitrogen without addressing other limiting factors will have no impact on the vegetation structure and carbon cycling and may instead harm vegetation by stressing it through nitrogen toxicity. However, similar studies at sites with lower background deposition below the critical load for peatlands have found similar limited impacts of nitrogen deposition (Bubier *et al.* 2007, Fritz *et al.*

2011), therefore suggesting that the increased background deposition at Whim Moss may not be a factor preventing the ecosystem responding to the additional nitrogen deposited on the experimental plots.

### **Relating vegetation surveying to carbon exchange**

The vegetation survey was found to be a reliable way of estimating the biomass and LAI of vascular species at Whim Moss. This allowed a quick and simple method to obtain vegetation biomass at the site without the need to destructively harvest the experimental site and exclude any future work on that area.

The method proved less successful when applied to mosses however. The visual estimation failed to quantify the density of the vegetation, therefore plots with the same estimated cover could in fact have a different amount of vegetation due to the spread of plant shoots. On varying topography, the vegetation shoots can be clustered very closely together or spread out. Another difficulty was judging at what depth in the plot the moss shifts from live vegetation, to dead vegetation and finally to soil. Due to the nature of peat formation and decay of mosses there is a gradual transition from live moss to formed peat (Rydin & Jeglum 2006, Clymo 1984), which makes it difficult to determine where different layers begin and therefore makes any judgement subjective. It is therefore likely that some variations in the mass of *Sphagnum*/mosses was due to varied stages of decomposition of the vegetation and differences in the depth to which the vegetation was removed.

The relationship found between LAI and NEE potentially provides a method to estimate the CO<sub>2</sub> exchange of a specific area by simply surveying the vegetation present. Analysers to measure CO<sub>2</sub> exchange can cost a significant amount of money and a large amount of time is required to obtain a sufficient number of measurements to understand the system. The time required to survey a particular area is very small and no specialist equipment is required, therefore it is possible to survey numerous sites in a short period without any specialist equipment.

The calculated LAI had a strong relationship with the modelled NEE, which was expected, as the amount of photosynthesis taking place will be linked to the amount of leaf area that the vegetation has available. The relationship with ER was also significant, however the LAI did not account for as much of the variation. This is likely due to the fact that there are numerous other sources of CO<sub>2</sub> that are not accounted for by LAI. These include vegetation respiration from woody sections and roots as well as CO<sub>2</sub> emissions from the organisms within the soil. It was clear that the method did not accurately take account of soil respiration when equation 3.8 was used to try to estimate soil respiration and gave a negative value. However, as the value was only -0.101 μmol m<sup>-2</sup> s<sup>-1</sup> it is possible that this is due to variation in the results and that increased numbers of measurements and improvements in the field measurements used to derive the equations may improve the accuracy of the estimate.

### **Future work opportunities**

As found in similar studies (Bubier *et al.* 2007, Saarnio *et al.* 2003, Fritz *et al.* 2011), addition of nitrogen by itself did not have a significant impact upon vegetation growth or CO<sub>2</sub> exchange. This is possibly due to growth remaining limited by additional nutrients such as phosphorus and potassium. As the Whim Moss experimental site has additional plots that include deposition of phosphorus and potassium as well as nitrogen, an expansion of these measurements to include these plots would provide an indication of whether the system was being limited by additional nutrients other than nitrogen.

Measurements of the impact would benefit from increased frequency of measurements over a longer period. Due to the number of analysers available for measurements, there were a limited number of measurements that could realistically be made in the time available. With additional analysers or multiplexers, it would be possible to acquire more data at more times around the year, which may identify effects of nitrogen deposition that are only detectable under certain environmental conditions.

There was concern about whether the background nitrogen deposition rate was sufficient to have impacted the control plots. If future manipulative experiments such as this are planned, then choosing a site away from significant levels of nitrogen deposition would negate concerns about the control plots. However similar studies by Bubier *et al.* (2007) and Fritz *et al.* (2011) at sites with low background nitrogen deposition found similar results. Carrying out vegetation and gas flux measurements at the site prior to the commencement of experimental nitrogen deposition at the site would provide increased confidence of whether the deposition had made a difference by comparing the change to that of control plots.

The vegetation survey and harvesting identified a possible method of estimating the vegetation biomass and CO<sub>2</sub> exchange without the need to destructively harvest the site being worked on. While the method appeared to work, there were noticeable areas for improvement, such as estimating soil respiration. This relationship would benefit from further measurements on an increased number of species to strengthen the data used to derive the equations used to calculate the biomass and NEE. The biomass estimates for mosses were not as good as for vascular species, possibly due to shoot density and variations in the vertical rate of decomposition. Significant improvements could be made by developing a better method of surveying mosses. The ER did not provide as good a fit as NEE, suggesting there are other factors impacting upon respiration. A further breakdown of the different sources of CO<sub>2</sub> emissions would aid the understanding and prediction of ER.

### **3.6 Conclusions**

Peatland ecosystems are subjected to significant levels of nitrogen deposition, with the effects on ecosystem functioning unknown. At Whim Moss an experimental nitrogen deposition study has been conducted for numerous years. Measurements have been made on plots with a range of nitrogen added to determine the impact on NEE, ER and vegetation growth.

It was found that there was no effect of nitrogen deposition on either NEE or ER. It is suggested that this might be due the ecosystem already having exceeded the critical load of nitrogen through background deposition or that the ecosystem is limited by other nutrients such as phosphorus or potassium and the increased levels of nitrogen are leading to nitrogen toxicity within the ecosystem.

There was also no impact of nitrogen deposition on vegetation biomass, possibly due to the same reasons for NEE and ER. However, a method was developed to estimate the vegetation biomass and LAI present in a plot from a non destructive vegetation survey. It was then possible to estimate the NEE from the LAI without the need for CO<sub>2</sub> analysers.

## **CHAPTER 4**

### **THE IMPACT OF BLOCKING MOORLAND OPEN DRAINS ON THE PEATLAND CARBON BALANCE**

## 4.1 Introduction

The UK has a small landmass and has historically relied upon imports in order to meet demand for food and raw materials. This has meant that there has always been pressure to increase the productivity of the land available for agriculture and forestry plantations (Holden *et al.* 2004). Peatland areas cover 10.9 % of the UK land surface (Montanarella *et al.* 2006), yet due to their high water tables and low nutrient content they do not provide a high agricultural yield. In the 19<sup>th</sup> – 20<sup>th</sup> Centuries there was significant peatland drainage, however after the Second World War there was intensive drainage of peatlands supported by government grants of up to 70 %, with the aim of increasing agricultural production (Holden *et al.* 2004). It is estimated that 1.5 million ha out of the 2.9 million ha of peat in the UK has been drained (Worrall *et al.* 2007). It has been suggested there is little impact on water table from open drains in upland areas with high rainfall and even at lower altitudes where the drains had more effect on water table, they have had little benefit for sheep or grouse (Coulson *et al.* 1990). With the practice not felt to be particularly effective and little evidence of increased productivity, it has largely ceased to be used as a management tool in recent decades (Holden *et al.* 2007a, Holden *et al.* 2004).

In upland peatlands drainage was typically implemented using open cut steep sided drains, known as grips, as seen in Fig. 4.1. Grips were either dug by hand or mechanically in a herring-bone pattern of smaller grips feeding a primary grip that would often feed into a natural watercourse. The size of grips and distance between them varies between sites, often from 0.5 – 2.0 m in depth and distances of between 3.5 – 14.0 m between grips (Holden *et al.* 2004).



Figure 4.1. An open moorland grip constructed on an upland blanket peatland in the North Pennines.

The drainage grips that were in place began to be associated with negative impacts such as erosion of the drains, as seen in Fig. 4.2, (Holden *et al.* 2007b), increased peat decomposition (Shantz & Price 2006) and changes in river flow patterns (Holden *et al.* 2006). As a result grips around the UK started to be blocked with a variety of aims, including habitat restoration, flood prevention and water quality improvement; with the UK Government aiming to have 95 % of SSSIs in a favourable or unfavourable recovering state (English Nature 2003). It is estimated that approximately £500 million has been spent in the north of England alone on blocking grips to reverse some of the damage caused (Ramchunder *et al.* 2009).



Figure 4.2. A grip that has been subjected to erosion that has increased the width and depth of the grip significantly. In some areas the entire depth of peat has been removed, exposing the rock at the base of the soil.

A variety of methods are used for blocking, as discussed in Armstrong *et al.* (2009). Frequently a dam is created across the drain to hold back the flow of water and raise the water table level within the drain and the surrounding area, or the drains can be collapsed by hand or by the use of heavy machinery. Typically the dams are constructed using peat, heather bales, metal, wooden or plastic sheets as seen in Fig. 4.3. A pool of water will be created behind the dam, which can either be left for vegetation to colonise naturally or vegetation can be added to speed up the restoration process. The grips blocked in this chapter were blocked using the technique of creating a peat dam every several metres along the grip.



Figure 4.3. Moorland grips after having been blocked, using plastic sheeting (left) and peat dams (right).

Restoration work is expected to have an impact on CO<sub>2</sub> and CH<sub>4</sub> fluxes as they are both believed to be influenced by the water table (Rydin & Jeglum 2006, Armstrong *et al.* 2009, Limpens *et al.* 2008). A lowered water table exposes a greater quantity of peat to oxygen, which provides the conditions for the soil to be decomposed, releasing CO<sub>2</sub>, and for CH<sub>4</sub> to be oxidised, reducing CH<sub>4</sub> emissions. As different moisture levels are favoured by different species, changing water table levels may also change the vegetation community structure, with subsequent impacts upon the productivity and carbon exchange of the land (Rydin & Jeglum 2006). It is unknown though how far the influence of grips extends and how much they alter these processes.

Bellamy *et al.* (2012) looked at the impact of grip blocking at a peatland in Scotland upon the surrounding vegetation. They found that unblocked grips had a higher level of species they considered to indicate drier degraded bog, such as *Calluna vulgaris*, *Mollinia caerulea* and species of *Hypnum*, in close proximity to the grip. They compared unblocked sites with two sites where grip blocking had taken place. At one site they found no impact of grip blocking, however at another they found an increase in species such as *Sphagnum cuspidatum*, *Sphagnum papillosum* and

*Eriophorum angustifolium*, which they considered to be indicators of a healthy wet peatland, in proximity to blocked grips.

A mesocosm experiment on cores extracted from two peatland sites vegetated primarily with species of *Sphagnum* and mosses found that lower water tables could reduce photosynthesis and increase soil and vegetation respiration (Blodau *et al.* 2004). The rate of photosynthesis was reduced from 48 to 27 mmol m<sup>-2</sup> d<sup>-1</sup> by lower water tables, whereas the CO<sub>2</sub> emissions were increased from 66 – 86 mmol m<sup>-2</sup> d<sup>-1</sup>. The CH<sub>4</sub> measurements were found to have no significant change between low and high water tables, which the authors suggested might be due the primary transport being due to ebullition, which was less pronounced in mesocosms than *in situ*.

Strack & Waddington (2007) made CO<sub>2</sub> and CH<sub>4</sub> field measurements comparing a site where the water table was drained by 20cm to a control. The drainage caused a significant increase in vascular vegetation cover from the second year after drainage. The study did not find that the reduction in water table level had any impact upon the NEE measurements, however there was a reduction in the CH<sub>4</sub> emissions from the drained site. Overall it was found that there was no significant difference in the mass of carbon emitted from the drained site to the control.

Van den Bos (2003) looked at flux measurements for agricultural peatlands in the Netherlands that had historically been drained and were being restored through drain blocking. They found that there was a slight increase in CH<sub>4</sub> emissions when the water table was raised. However, they found that raising the water table reduced the CO<sub>2</sub> emissions from the site and overall the rewetting of the site reduced greenhouse gas emissions as the increase in CH<sub>4</sub> was outweighed by the reduction in emissions of CO<sub>2</sub> from the site.

A study by Komulainen *et al.* (1999) measured the effect of restoring the water table on CO<sub>2</sub> at a peatland in Finland. It was found that the water table rose by 20 – 25 cm and there was an increase in cover of *Sphagnum balticum*, *Sphagnum fuscum*, *Polytrichum strictum*, *Andromeda polifolia*, *Vaccinium oxycoccos* and *Vaccinium microcarpum*. There was a reduction in *Cladonia* species at the site and *Calluna vulgaris* located in hollows at the site began to die. On plots with no vegetation

cover it was found that CO<sub>2</sub> respiration was decreased from 51 – 310 mg m<sup>-2</sup> h<sup>-1</sup> in undrained sites to 36 – 290 mg m<sup>-2</sup> h<sup>-1</sup> in rewetted sites. At sites with vegetation the CO<sub>2</sub> efflux also decreased, however there was no treatment effect on CO<sub>2</sub> assimilation.

At a Scottish forested peatland Yamulki *et al.* (2013) examined the impact restoring the water table at a drained site. They found that higher water table levels led to increased annual CH<sub>4</sub> emissions. However, drained sites were found to have higher emissions of CO<sub>2</sub> than those with restored water tables. Overall it was found that restoring the peatland reduced greenhouse gas emissions compared with a drained afforested peatland.

Strack & Zuback (2013) measured the annual carbon balance at a Canadian peatland 10 years after drains had been restored. They compared a pristine site, restored site and a site still with active drainage in place. They found that the restored site had the highest CO<sub>2</sub> uptake of the three sites, while the drained site had the lowest and was a source of CO<sub>2</sub> during the growing season. There was no significant difference in CO<sub>2</sub> respiration between the pristine and restored sites, however they were significantly higher at the drained site. There was no difference in CH<sub>4</sub> emissions between drained and restored sites, but the pristine site had significantly higher CH<sub>4</sub> emissions. DOC concentrations in fluvial runoff were also reduced at the restored site.

In addition to land-atmosphere exchanges of carbon, carbon can be lost through water outflow from the peatland. Turner *et al.* (2013) found that the blocking of grips could reduce the amount of carbon that was being removed from a peatland system. The key driver for this change in carbon export was determined to be a reduction in the water export from the site. Drain blocking in northern England has been found to reduce the concentration of DOC in exported water by 69 % and water colouration by 62 %, indicating grip blocking has positive impacts for the fluvial carbon loss and water colour treatment by water utility companies (Wallage *et al.* 2006).

It can be seen from the studies cited that the measured impacts of drainage and of water table restoration can have a range of effects upon the water table, vegetation and carbon balance. Previous studies have been carried out at varying locations in

different countries, subjected to a range of environmental and physical conditions that may impact the extent of drainage on the ecosystem. Differences in vegetation, soil chemical and physical structure and microbial communities between sites will account for some variation in how the ecosystem will respond to restoration work. In addition, the methods used to construct the grips and subsequently restore the site may also play a part. As there is variation both in the size and frequency with which grips were installed at sites, this will influence how effective they were at draining the land. At drained sites, some grips have become partially or completely blocked due to the collapse of the grip or an accumulation of vegetation. Restoration work at such sites may not be as effective, as the influence of the grips is already reduced. Finally, the efficacy of the method used to block the grips might affect to what extent the peatland is impacted by the restoration work.

## 4.2 Aims

This chapter aims to investigate the impact of grips upon the water table and land-atmosphere carbon exchange. It is hypothesised that the water table will be lower in proximity to unblocked grips, whereas when the grips are blocked there will be no significant difference in water table level at different distances from the grip. It is hypothesised that lower water tables in proximity to the grips will result in reduced methane emissions, but a reduction in the NEE uptake due to increased CO<sub>2</sub> emissions. The field measurements commenced in 2010, the year prior to blocking taking place and continued in the same manner for the year after the grips were blocked at the beginning of 2011, to develop a comparison between the ecosystem behaviour before and after the restoration. It aims to establish the scale at which grips affect the surrounding area and the magnitude of this effect.

## 4.3 Methods

### 4.3.1 Field site

The field site is located in the North Pennines Area of Outstanding Natural Beauty in the north of England, an area encompassing moorlands and dales. The North Pennines contain 27 % of the blanket bog in England and are important habitats for newts, slow-worms, red squirrels, dunlin, golden plover, black grouse and merlin. The peatlands in the North Pennines are the most heavily drained in England and by the 1980s there were around 9,400 km of drains installed (North Pennines AONB).

The site is located at national grid reference NY907476 and is part of an estate managed for grouse shooting, with regular burning of vegetation. The specific site measurements took place on was not subject to burning, however it was open to grazing by sheep. The site is located 470 m above sea level, topography gently sloping and vegetation largely consisted of *Calluna vulgaris*, *Eriophorum vaginatum* and species of *Sphagnum* and mosses as seen in Fig. 4.4. The mean air temperature at the site during 2010 – 2011 was 7.1 °C and mean annual precipitation was 914.1 mm.



Figure 4.4. View of the field site from the east, with a measurement transect visible in the foreground and CO<sub>2</sub> measurements in progress.

The field site had a large number of grips present, six of which were selected for use in the study as shown in Fig. 4.5. For the first year of the study all grips were left unblocked as measurements were carried out to establish a baseline for the grips in an unblocked state. At the end of the first year, three grips were blocked using extracted peat to form a dam within the grip to hold back water as described in Armstrong *et al.* (2009). The remaining three grips were left in their unblocked state to act as control plots to compare to the blocked grips. Once the blocking had taken place the measurements continued on the plots for a further year.



Figure 4.5. An aerial photograph of the field site showing the grip locations. The six grips at which measurements were made are marked in red.

### **4.3.2 Water table measurements**

A perpendicular transect was positioned across each grip along which measurements at a set distance from the grip could be made as seen in Fig. 4.6. There were 11 dipwells positioned on each side of the grip, the first at 0.5 m from the edge of the grip and then every 0.5 m up to 5 m away from the grip edge. A final dipwell was placed 7.5 m from the grip edge to identify if the water table was still rising at that distance away from the grip. This would allow additional dipwells to be installed if those placed within 5 m of the grip were insufficient to identify where the influence of the grip ended. Water table measurements were made manually on every site visit using a tape measure as described in the methods chapter. In addition, PDCR 1830 pressure transducers (Campbell Scientific) were installed in four extra dipwells to continuously monitor the water table at 1 m and 5 m away from two grips.



Figure 4.6. A transect of dipwells and chamber bases across an unblocked grip, with CO<sub>2</sub> measurements in progress on the far side of the grip.

### 4.3.3 CO<sub>2</sub> and Methane measurements

There were 30 chamber bases used at the site, which were permanently positioned at 1, 3 and 5 metres away from the grip edge as seen in Figs. 4.4 and 4.6. In between measurements the chamber bases were left at the site to avoid repeatedly disturbing the vegetation by removing and reinstalling the bases.

The methane measurements were made using the closed chamber method described in Chapter 2. There were 15 chamber lids available for use, so methane measurements were made in two sets of measurements during a single day. Samples were taken every 20 minutes once the chamber was enclosed. Air samples were transported to the laboratory and analysed with 48 hours of being sampled.

CO<sub>2</sub> flux measurements were made using CIM IRGAs (PP Systems) as described in Chapter 2. During measurements one of the CIMs would be used with the darkened chamber in order to measure ER, while up to four other CIMs, depending on availability, were used with clear chambers in order to measure NEE. To make the

measurements, the available gas analysers were started randomly spread out at different measurement plots across the site early in the morning. They were set to record an average flux measurement every two minutes and remained on an individual plot for between 15 – 20 minutes at one time. During the day they would be rotated so that all of the plots were measured several times during the day to obtain sufficient flux measurements.

For the period that measurements were made a CR10X datalogger (Campbell Scientific) was used to record average environmental variables at 1 minute intervals. The datalogger was synchronised to the internal clocks on the CO<sub>2</sub> analysers prior to sampling to permit environmental data to be matched up to the relevant fluxes. Air temperature was monitored using a 107 thermistor probe located within a radiation shield (Campbell Scientific) and PAR was monitored using a PAR Quantum sensor (Skye Instruments). These sensors were located in the centre of the experimental area and positioned approximately 1 metre above the ground. In addition each CO<sub>2</sub> analyser had a CR200 datalogger (Campbell Scientific) attached to it with a 109 thermistor probe (Campbell Scientific) which was used to record the soil temperature adjacent to individual plots.

Measurement visits to the field site were carried out over 2010 – 2011. In 2010, the year prior to blocking four visits were made to the site between March – November to establish the baseline measurements. The blocking of the three treatment grips was carried out over the winter of 2010 – 2011. During 2011 five measurement visits were carried out between July – October.

#### 4.3.4 Data analysis and statistics

Analytical software packages Minitab 16 (Minitab Inc.) and GenStat 14 (VSN International) were used to perform analysis of the data. A one way ANOVA was used to identify significant differences in the water table depth at different distances from the grip. As measurements of NEE, ER and CH<sub>4</sub> flux did not take place simultaneously across all plots, the measured fluxes were related to recorded environmental measurements at the site in order to determine the flux response of the plot.

NEE measurements were related to PAR using the equation  $NEE = A + B \times (R^{PAR})$ , developed within GenStat to model vegetation responses to solar radiation. ER and CH<sub>4</sub> flux were related to water table depth using a linear regression  $ER \text{ or } CH_4 = A + B \times WT$ . The constants derived from these relationships and the flux values calculated by these relationships were tested with a T-Test and ANOVA to determine if there were differences between the treatments and the distance from the grip.

## 4.4 Results

### 4.4.1 Water table

Water table measurements varied during the study period ranging from the lowest measurement of 45.6 cm below the soil surface to a highest measurement of 6.1 cm above the soil surface. The average water table depth from the manual measurements taken during site visits was 6.8 cm below the soil surface. The water table level was very responsive to rainfall as seen in Fig. 4.7. During periods of no rainfall the water table steadily dropped, quickly rising in response to rain.

There was slightly higher rainfall during the second year of measurements. Between 22 March – 31 December 2010 total rainfall was 873.6 mm, while between 01 January – 22 October 2011 total rainfall was 954.6 mm. The average temperature was similar between the two years, being 7.5 °C in the first year and 6.3 °C in the second, however the periods that measurements were recorded at the site did not cover equivalent months across both years.

The automated sensors shown in Fig. 4.7. showed that throughout both years, sensors located near to the grip had a lower water table depth than those positioned further away. There was also visibly a greater variation in the range of water table depths for sensors near unblocked grips. As seen in Fig. 4.7., Graph C, the water table depth measured by the sensor at 5 m from the grip varied between 5.5 cm above the soil to 25.7 cm below the soil, whereas measurements 1 m from the grip varied from 6.3 cm above the soil to 58.8 cm below the soil.

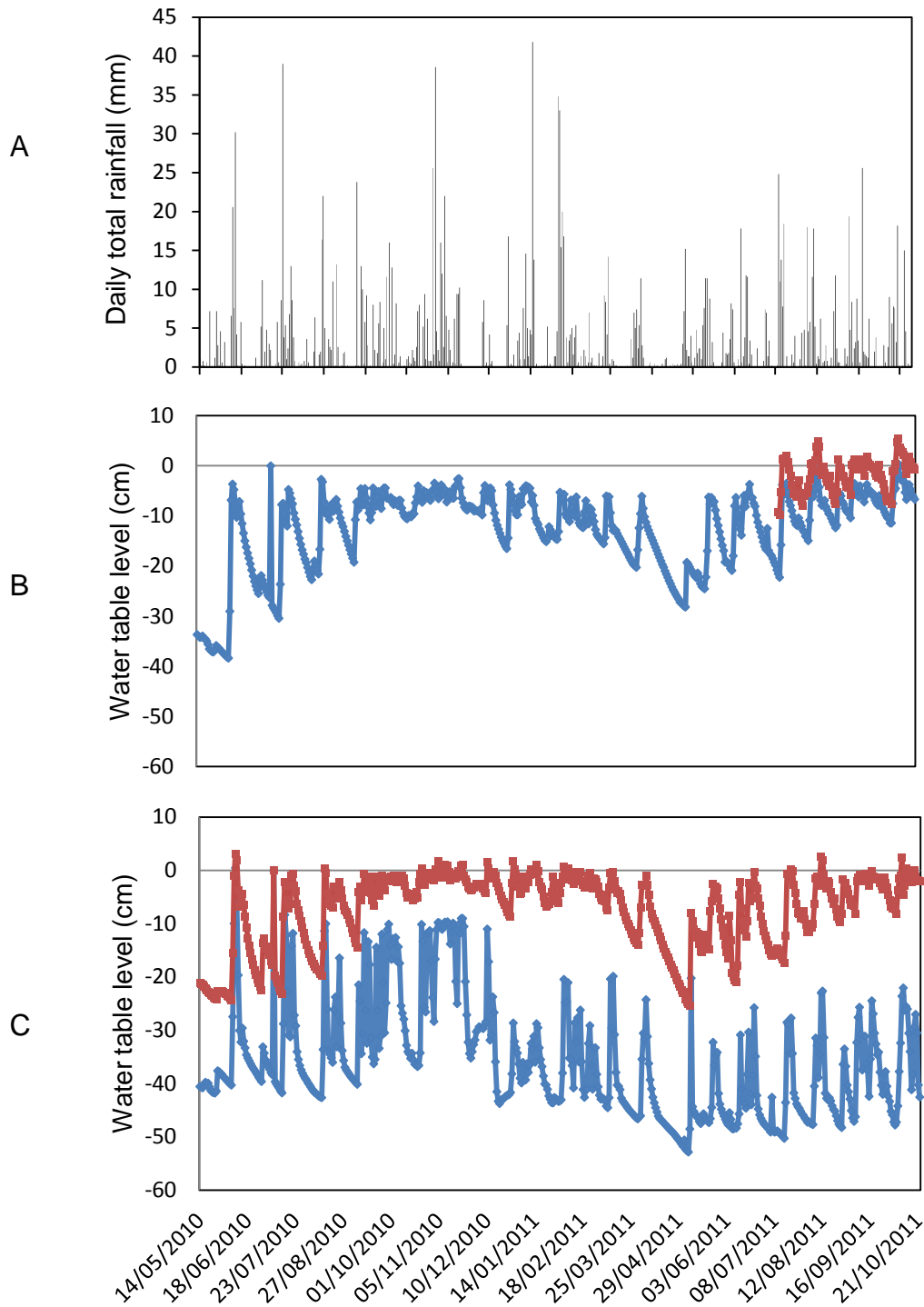


Figure 4.7. The total daily rainfall (Graph A) and the two grips monitored with automated water depth sensors. Blue lines indicate the water depth one metre from the grip, red lines indicate 5 metres. Graph B in the centre shows data from a grip blocked in January 2011, whereas Graph C at the bottom shows a control grip that remained unblocked for the duration of measurements.

Prior to the blocking taking place the influence of the grips appeared limited to the immediate vicinity of the grip as seen in Fig. 4.8. For both control and treatment grips the water table depth 0.5 m from the grips was significantly lower than further away from the grip (ANOVA,  $P < 0.001$ ). The mean depth was 6.7 cm lower in dipwells at 0.5 m than dipwells further away from the grips. The distribution of measurements was greater for dipwells positioned 0.5 m from the grip edge.

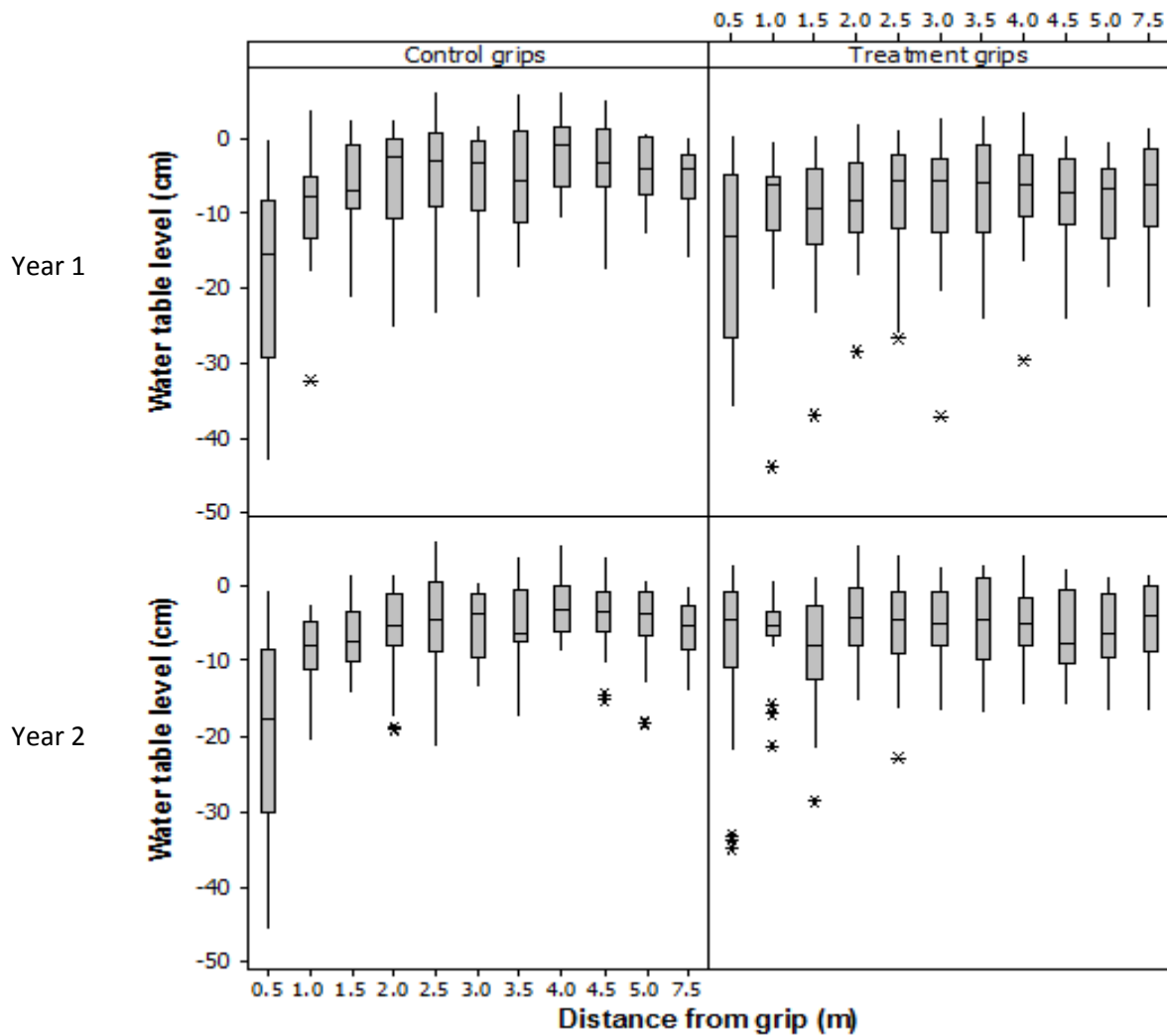


Figure 4.8. Water table depth around the control and treatment grips during the first and second years of measurements. During the first year, treatment grips were in an unblocked state, blocking taking place in between the first and second years of measurements. The box represents the interquartile range, with the mean indicated by a horizontal line within the box. The whiskers represent the upper and lower 25 % of the distribution. Outliers are indicated by asterisks.

In the second year of measurements after blocking had taken place the control grips were still significantly lower at 0.5 m from the grip ( $F = 15.77$ ,  $P < 0.001$ ), whereas the treatment grips were not significantly different at any distance from the grip ( $F = 0.093$ ,  $P = 0.504$ ) as seen in Fig. 4.8. The mean water table grip of dipwells positioned 0.5 m by the control grips was 10.9 cm lower than the next lowest mean at 1 m from the grip edge, whereas the mean of the treatment grips 0.5 m from the grip edge were within the same range as the water table at all distances from the grip edge. However it is noted that the treatment grips in year 2 had a greater number of outliers closer to the grip.

#### **4.4.2 NEE flux measurements**

In the first year of NEE measurements to measure the net CO<sub>2</sub> flux, the NEE fluxes ranged from  $-7.54 \mu\text{mol m}^{-2} \text{s}^{-1}$  to  $4.45 \mu\text{mol m}^{-2} \text{s}^{-1}$  while in the second year they ranged from  $-8.79 \mu\text{mol m}^{-2} \text{s}^{-1}$  to  $4.80 \mu\text{mol m}^{-2} \text{s}^{-1}$ . As seen in Figs. 4.9 and 4.10 NEE fluxes were influenced by the level of PAR to varying degrees on different plots across both years of measurements.

As measurements were not made simultaneously on all plots, direct comparison of measurements was difficult, therefore exponential lines were fitted using a model developed by Genstat to examine vegetation light response ( $\text{Flux} = A + B \times R^{\text{PAR}}$ ) were used to determine the response of the fluxes at each individual plot to PAR, as shown in Appendix A. This accounted for differences that existed in environmental conditions at the time of individual plot measurements and enabled comparison between plots.

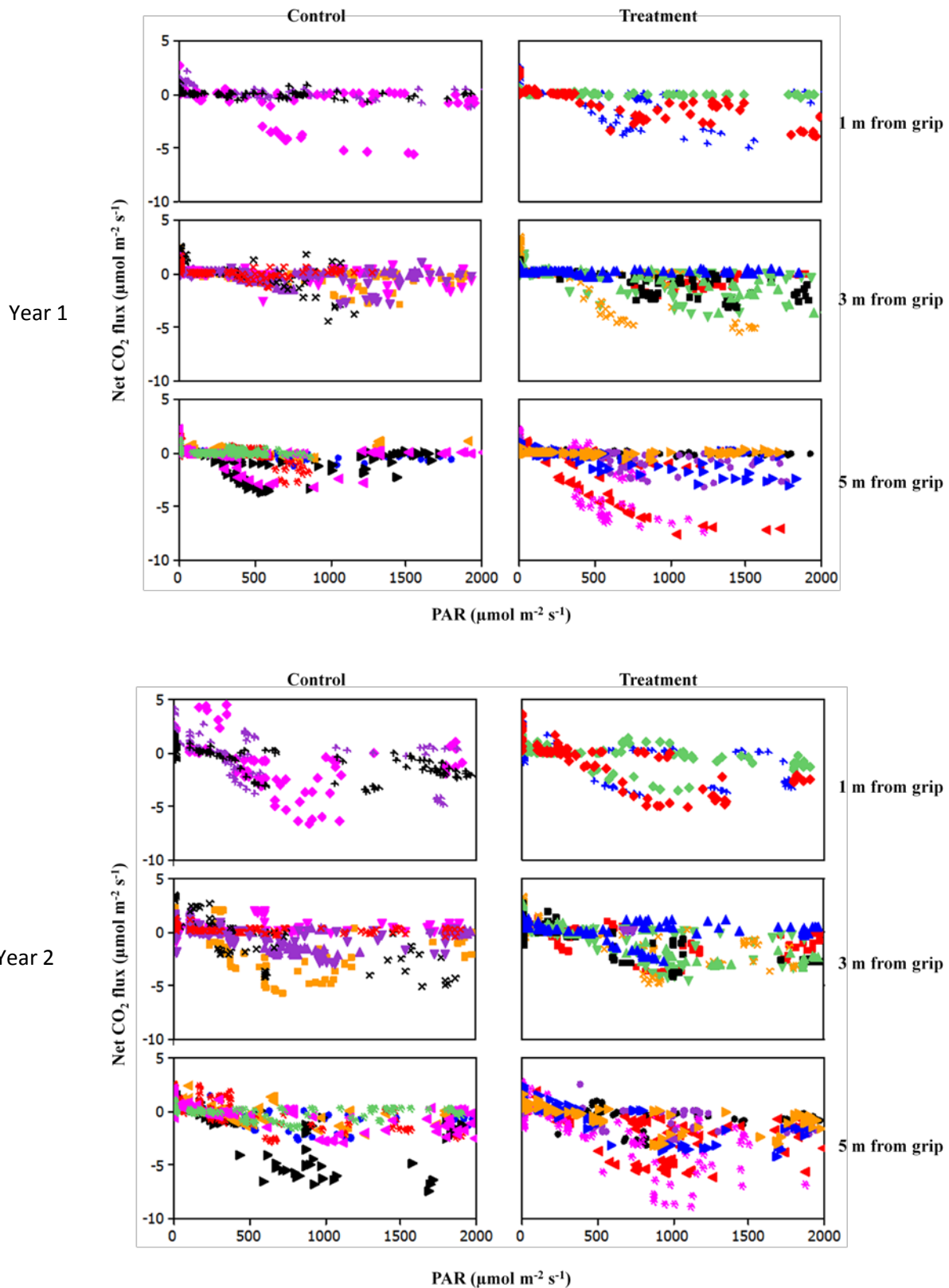


Figure 4.9. The relationship between NEE and levels of PAR prior to and post blocking. Separate panels show relationships for control and treatment plots at different distances from the grips. The different symbols on the graphs relate to flux measurements for different measurement plots.

The components of the flux equation ( $\text{Flux} = A + B \times R^{\text{PAR}}$ ) were examined, a T-Test found there was no significant difference between the treatments for the components of the fitted lines for either year, Year 1 R ( $T = 0.30, P = 0.764$ ), Year 1 B ( $T = 0.54, P = 0.591$ ), Year 1A ( $T = -0.48, P = 0.634$ ), Year 2 R ( $T = -0.05, P = 0.959$ ), Year 2 B ( $T = -0.31, P = 0.756$ ), Year 2 A ( $T = 0.38, P = 0.709$ ). The fitted lines were used to estimate the NEE for the individual plots at a range of PAR levels as shown in Table 4.1.

Table 4.1. Mean NEE fluxes ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) calculated from the fitted exponential lines for control and treatment plots for both years of measurements at a range of PAR levels. Differences between the control and treatment groups have been tested with a T-test.

PAR $\mu\text{mol m}^{-2} \text{s}^{-1}$	2010 (prior to treatment)			
	Control	Treatment	T	P
300	-0.205	-0.602	1.73	0.101
600	-0.704	-1.430	1.67	0.111
900	-1.220	-2.040	1.39	0.177
1200	-1.860	-2.510	0.83	0.411
1500	-2.820	-2.890	0.06	0.955

PAR $\mu\text{mol m}^{-2} \text{s}^{-1}$	2011 (post blocking)			
	Control	Treatment	T	P
300	-0.484	-0.557	0.37	0.715
600	-1.290	-1.430	0.39	0.699
900	-1.77	-1.94	0.36	0.723
1200	-2.08	-2.25	0.30	0.766
1500	-2.30	-2.45	0.23	0.816

Fig. 4.10. shows typical mean modelled fluxes for control and treatment plots at a level of PAR of  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ , over the first and second year of measurements. During the first year of measurements there was no significant difference between fluxes based on their distance away from the grip. The lowest P value from levels of PAR modelled was at a PAR value of  $100 \mu\text{mol m}^{-2} \text{s}^{-1}$  using a one-way ANOVA ( $F = 2.55, P = 0.096$ ). This level of PAR was also the only level at which there was any correlation between the flux and the distance from the grip ( $r = -0.399, P = 0.029$ ) from the modelled fluxes. This indicated that at this low level of PAR, there was an

increased level of CO<sub>2</sub> exchange from the atmosphere to the soil further away from the grip.

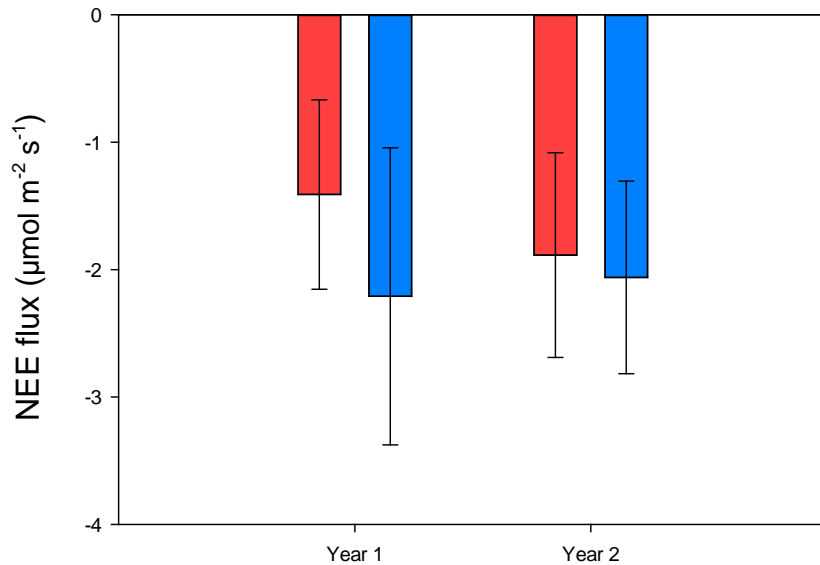


Figure 4.10. Modelled mean NEE fluxes at PAR level 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . Bars for control plots are marked red and treatment bars marked blue. Error bars indicate 95 % confidence intervals.

During the second year of measurements the control grips again showed no significant differences between fluxes based on distance from the grip, the lowest P value was again at 100  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR, ( $F = 1.65$ ,  $P = 0.233$ ). There was also no correlation between the flux and the distance from the grip, the closest to significant being at 100  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR, ( $r = -0.321$ ,  $0.244$ ). Blocked grips also showed no significant difference in flux between distances from the grip, the lowest P was at 300  $\mu\text{mol m}^{-2} \text{s}^{-1}$  ( $F = 0.45$ ,  $P = 0.647$ ). There was no significant correlation either with distance, the closest being at 100  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR ( $r = -0.082$ ,  $P = 0.773$ ).

As the water table measurements had indicated that the impact of unblocked grips was limited to the immediate vicinity of the grip, the flux measurements from plots at 1 m distance from the grip were examined separately. However there was no significant difference between the treatments (at 100  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR,  $T = 0.67$ ,  $P = 0.550$ ) and no significant difference between years for the control plots (at 100  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR,  $T = -1.52$ ,  $P = 0.267$ ) or the impact plots (at 400  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR,  $T = 0.87$ ,  $P = 0.450$ ).

### 4.4.3 Ecosystem respiration measurements

During the period that CO<sub>2</sub> respiration measurements were made at the site, the average flux was 0.78 μmol m<sup>-2</sup> s<sup>-1</sup>. The maximum respiration flux measured at the site was 4.14 μmol m<sup>-2</sup> s<sup>-1</sup>. As seen in Fig. 4.11. the CO<sub>2</sub> respiration for individual plots was influenced by the water table in that location, with a lower water table typically associated with higher CO<sub>2</sub> emissions.

As with NEE measurements, ER measurements were not made simultaneously across all plots, therefore in order to compare plots the ER measurements for each plot were fitted using a linear regression line against the measured water table depth (Flux = A + B x WT). This accounted for changes in environmental conditions between when measurements were made.

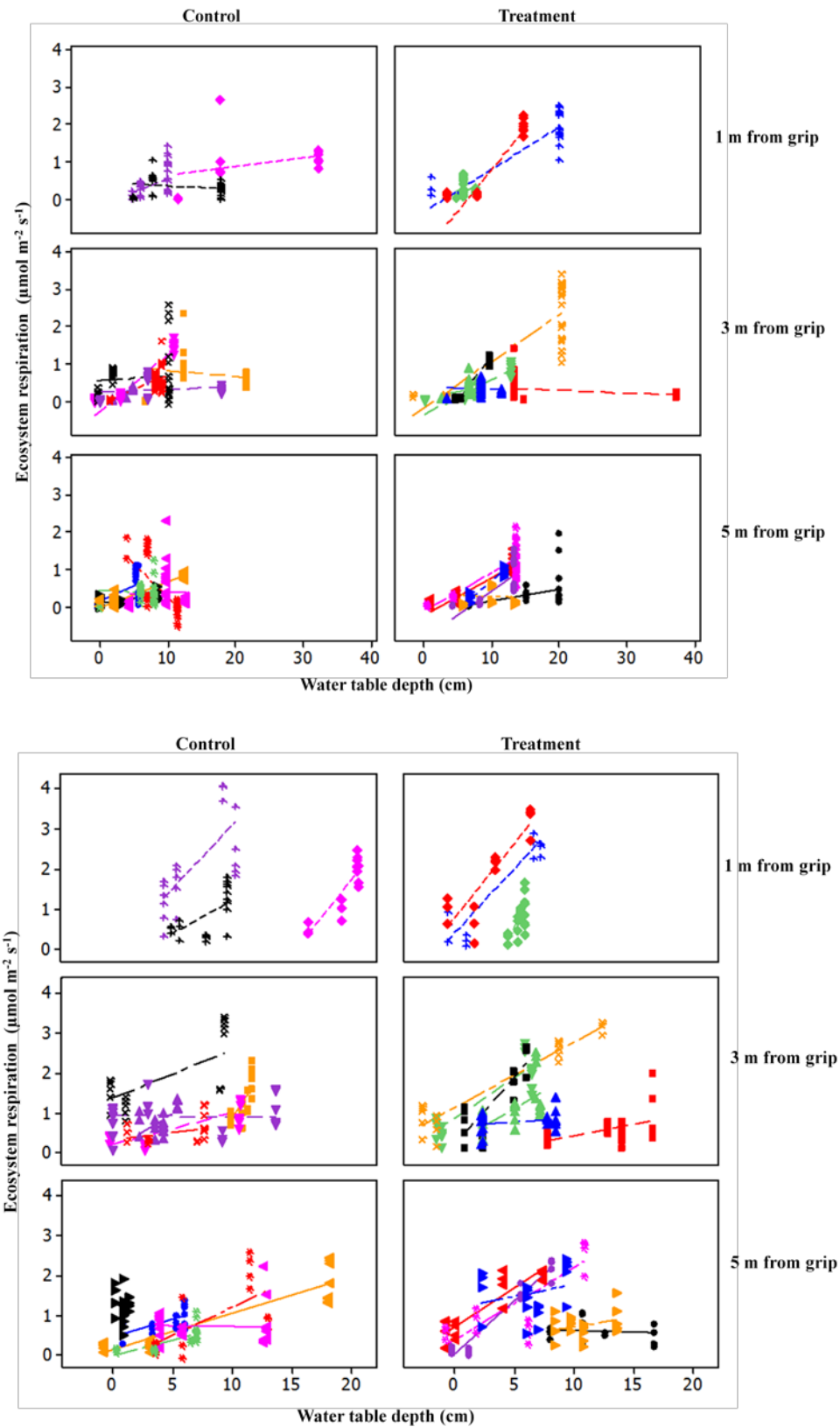


Figure 4.11. Ecosystem respiration measurements plotted against measured water table depth. The different symbols on the graphs relate to flux measurements for individual measurement plots and linear regression lines have been fitted. All grips were in an unblocked state during the first year and treatment grips were blocked in between the first and second years of measurements.

A T-Test found there was no significant difference between the treatments for the components of the fitted regression lines for either year, Year 1 A (T = -0.94, P = 0.357), Year 1 B (T = 0.14, P = 0.886), Year 2 A (T = -1.82, P = 0.081), Year 2 B (T = 1.70, P = 0.101). The fitted lines were also used to estimate the CO<sub>2</sub> respiration for the individual plots at a range of water table depths. As shown in Table 4.2 and Fig. 4.12. there was no significant difference in ER flux between the control and treatment plots at any of the water table depths modelled.

Table 4.2. Mean CO<sub>2</sub> respiration fluxes ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) calculated from the fitted lines for control and treatment plots. Difference between groups was tested using a T-test.

Water table depth (cm)	2010 (Prior to blocking)			
	Control	Treatment	T	P
5	0.432	0.310	1.09	0.289
10	1.011	0.913	0.42	0.680
15	1.589	1.510	0.19	0.850
20	2.170	2.120	0.09	0.927

Water table depth (cm)	2011 (Post blocking)			
	Control	Treatment	T	P
5	0.069	-0.312	1.73	0.095
10	1.022	1.146	-0.66	0.518
15	1.980	2.600	-1.41	0.171
20	2.93	4.06	-1.54	0.135

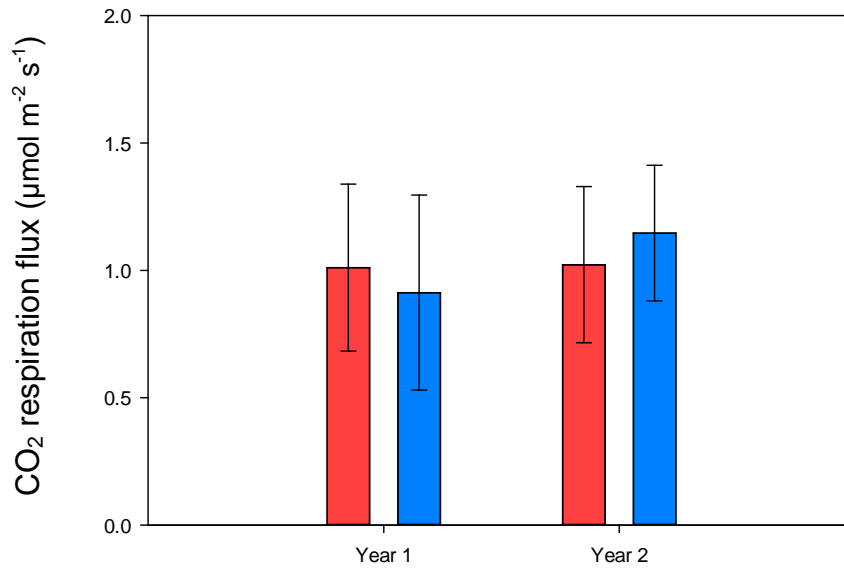


Figure 4.12. Mean CO<sub>2</sub> respiration measurements modelled at a water table depth of 10 cm. Bars for control plots are marked red and treatment bars marked blue. Error bars indicate 95 % confidence intervals.

The CO<sub>2</sub> respiration increased from the first year to the second in both the control and the treatment plots. Control plot emission increased on average by 25.5 % while treatment plots increased by 73.0 %. The increase in control emissions was not significant ( $T = 1.43$ ,  $P = 0.167$ ), whereas the treatment emissions were significantly higher ( $T = -2.90$ ,  $P = 0.008$ ).

In the first year, prior to blocking of the grips, the flux correlated with distance ( $r = -0.379$ ,  $P = 0.039$ ), the flux being lower further away from the grip. During the second year there was no correlation between the flux and the distance from the grip either for the control plots ( $r = -0.436$ ,  $P = 0.104$ ) or the treatment plots ( $r = -0.380$ ,  $P = 0.162$ ).

#### 4.4.4 Methane measurements

During the study period the average CH<sub>4</sub> flux measured was 8.1 nmol m<sup>-2</sup> s<sup>-1</sup>, ranging from a low of -3.6 nmol m<sup>-2</sup> s<sup>-1</sup> to a maximum of 68.9 nmol m<sup>-2</sup> s<sup>-1</sup>. As seen in Fig. 4.13. the CH<sub>4</sub> flux was influenced by the water table depth. As CH<sub>4</sub> measurements were not made simultaneously, in order to compare plots the CH<sub>4</sub> measurements for each plot were fitted with linear regression lines against the measured water table depth (Flux = A + B x WT). A T-Test of the components of the regressions found no significant differences between treatments in the first year prior to blocking, A (T = -0.15, P = 0.882), B (T = 0.18, P = 0.856) and in the second year post blocking, A (T = 0.35, P = 0.729), B (T = -0.95, P = 0.357).

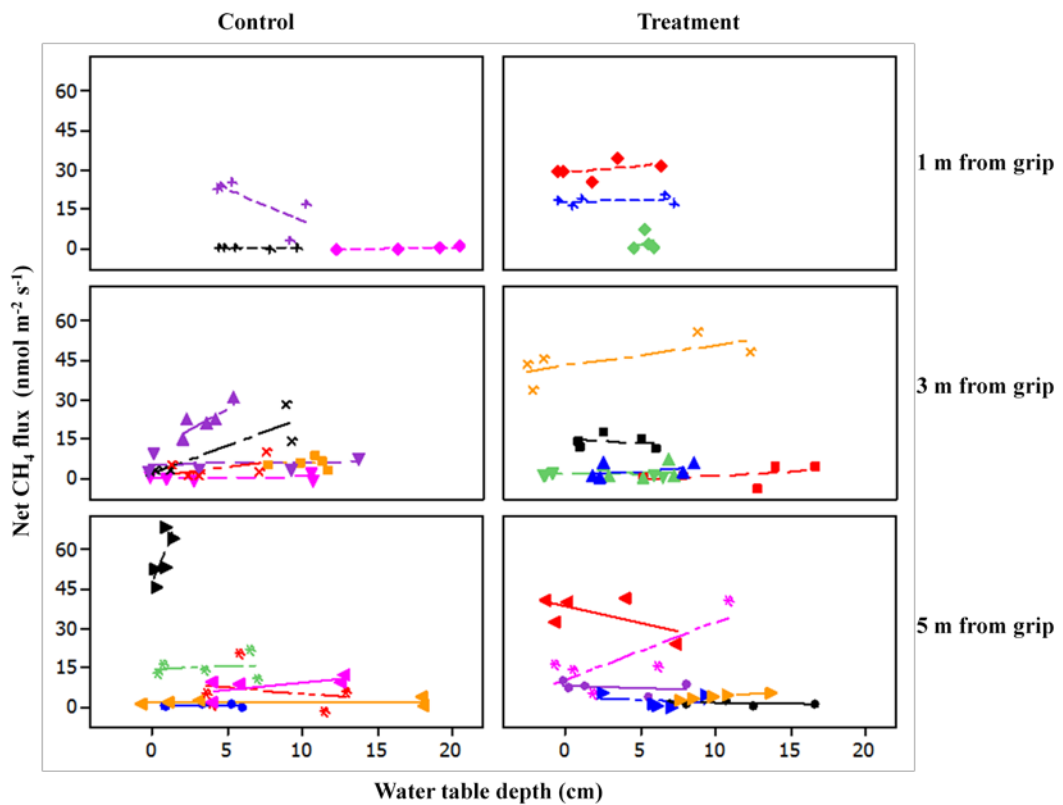
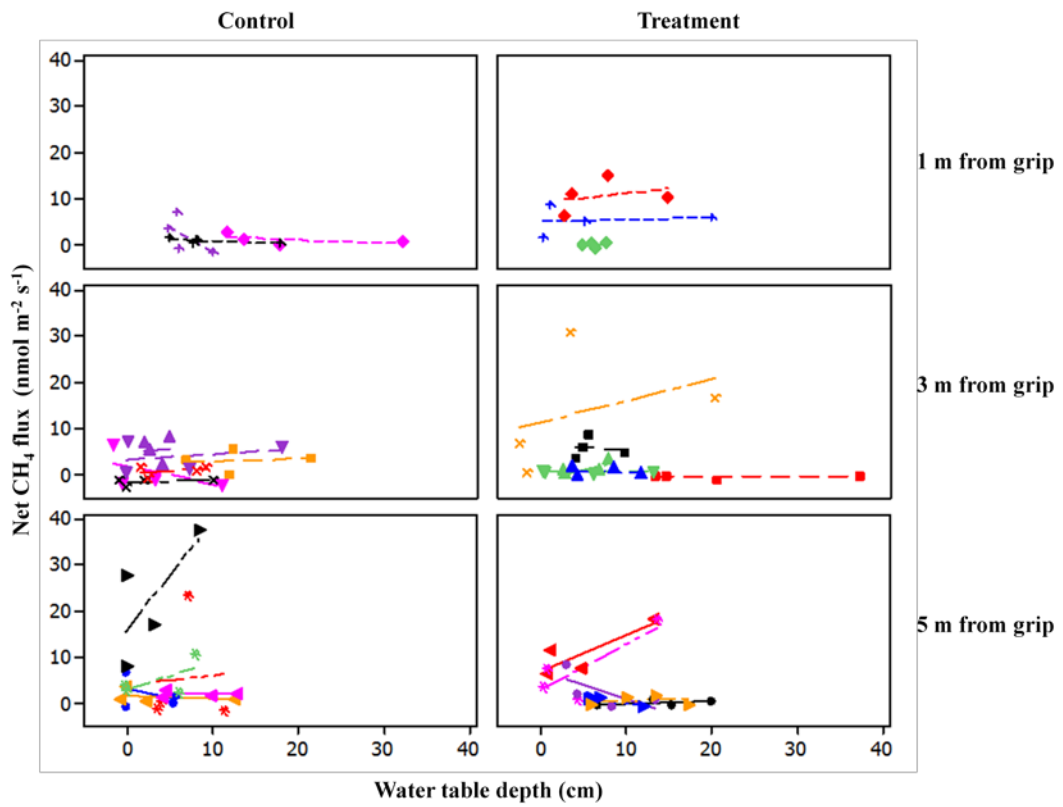


Figure 4.13. Methane fluxes plotted against water table depth with individual linear regression fitted lines fitted. The different symbols on the graphs relate to flux measurements for individual measurement plots and linear regression lines have been fitted.

The fitted regressions shown in Fig. 4.13. were used to estimate the net flux of the measurement plots at varying water table levels. As shown in Table 4.3 and Fig. 4.14. there was no significant difference between the modelled CH<sub>4</sub> fluxes at any water table depth they were modelled for.

Table 4.3. Mean CH<sub>4</sub> fluxes (nmol m<sup>-2</sup> s<sup>-1</sup>) calculated from the fitted lines for control and treatment plots. Difference between groups was tested using a T-test.

Water table depth (cm)	Year 1 (Prior to blocking)			
	Control	Treatment	T	P
0	3.75	3.53	0.15	0.882
10	4.70	4.86	-0.05	0.958
20	5.60	6.19	-0.11	0.914

Water table depth (cm)	Year 2 (Post blocking)			
	Control	Treatment	T	P
0	9.20	11.1	-0.35	0.729
10	21.5	13.8	0.59	0.564
20	33.8	16.5	0.76	0.459

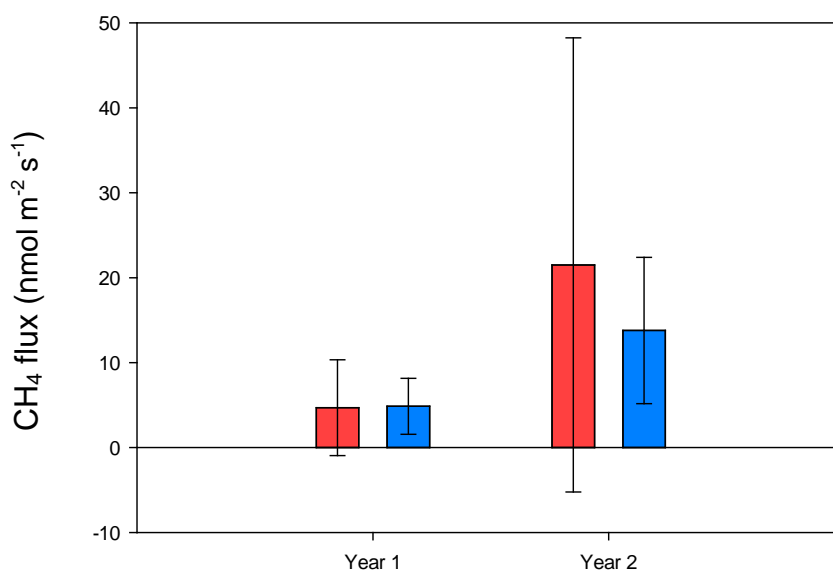


Figure 4.14. Mean CH<sub>4</sub> measurements modelled at a water table depth of 10 cm. Bars for control plots are marked red and treatment bars marked blue. Error bars indicate 95 % confidence intervals.

It was noted that methane fluxes increased at both control and treatment plots between the first and second year as seen with ER and the range of fluxes increased. The average fluxes at the control sites increased by 1.54 times, however this was not a significant increase ( $T = -1.59$ ,  $P = 0.131$ ). The treatment site average methane flux increased by 1.95 times from the first to the second year, a significant increase ( $T = -2.17$ ,  $P = 0.045$ ).

There was found to be no correlation between the methane fluxes and distance away from the grip in the first year ( $r = 0.159$ ,  $P = 0.402$ ) or in the second year measurements for the control grips ( $r = 0.319$ ,  $P = 0.247$ ) or the treatment grips ( $r = -0.142$ ,  $P = 0.612$ ). This suggested that there was no treatment effect of the grip.

#### 4.4.5 Vegetation biomass and LAI estimation

The vegetation survey at the site gave estimates of the cover and height for a number of vegetation species at the site. The equations (3.1, 3.2, 3.3, 3.4 & 3.5) derived from measurements made at Whim Moss in Chapter 3 were used to estimate the biomass present in the plots in Newbiggin based on the vegetation survey carried out at the site. The estimated mass of the main species present at the site is shown in Table 4.4.

Table 4.4. Estimated mean biomass calculated to be present in experimental plots by treatment.

Vegetation	Control (g m <sup>-2</sup> )	Treatment (g m <sup>-2</sup> )	T-Value	P
<i>Calluna</i>	500.9	561.3	0.60	0.553
<i>Calluna</i> green	351.1	362.5	0.25	0.806
<i>Eriophorum</i>	151.3	147.2	-0.09	0.932
Moss & <i>Sphagnum</i>	1021.2	1107.5	1.09	0.292
Total vegetation	1954.0	2129.4	1.30	0.205

As shown in Fig. 4.15. there were no differences between control and treatment plots for all vegetation and individual species mass when examined with a T-test: Total vegetation ( $T = -1.30$ ,  $P = 0.205$ ), Total *Calluna* ( $T = 0.60$ ,  $P = 0.553$ ), Green *Calluna* ( $T = 0.25$ ,  $P = 0.806$ ), *Eriophorum* ( $T = -0.09$ ,  $P = 0.932$ ), Moss and

*Sphagnum* ( $T = 1.09$ ,  $P = 0.292$ ). The majority of the biomass within plots was due to mosses, with *Calluna vulgaris*, the second most significant vegetation biomass.

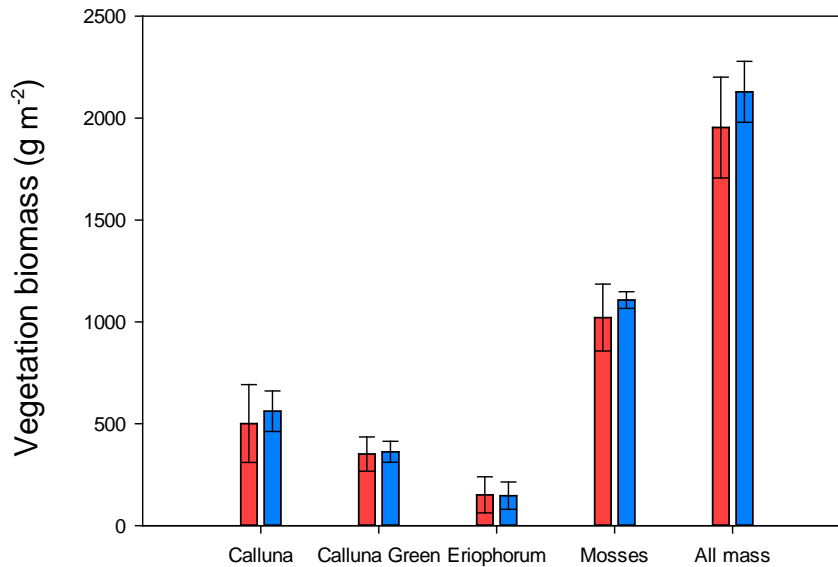


Figure 4.15. Bar chart showing the mean calculated biomass of primary vegetation types based on the vegetation survey. Bars for control plots are marked red and treatment bars marked blue. Error bars indicate 95 % confidence intervals.

When vegetation was examined for a correlation between mass and distance from the grip there was no significant relationship for *Eriophorium* or moss and *Sphagnum*. *Eriophorium*: Control ( $r = 0.147$ ,  $P = 0.601$ ), Treatment ( $r = 0.004$ ,  $P = 0.990$ ). Moss and *Sphagnum*: Control ( $r = -0.362$ ,  $P = 0.204$ ), Treatment ( $r = 0.067$ ,  $P = 0.812$ ). Fig. 4.16. shows the relationship between biomass and distance from the grip for *Calluna* Total and Green and for all vegetation. Total *Calluna* mass showed an almost significant correlation with distance for both control ( $r = -0.510$ ,  $P = 0.052$ ) and treatment ( $r = -0.488$ ,  $P = 0.065$ ) plots. Green *Calluna* mass had a significant correlation with distance for the Control ( $r = -0.539$ ,  $P = 0.038$ ) and treatment ( $r = -0.592$ ,  $P = 0.020$ ). For Total vegetation, while there was no correlation with distance for control plots ( $r = -0.343$ ,  $P = 0.211$ ), there was a significant correlation for treatment plots ( $r = -0.523$ ,  $P = 0.045$ ).

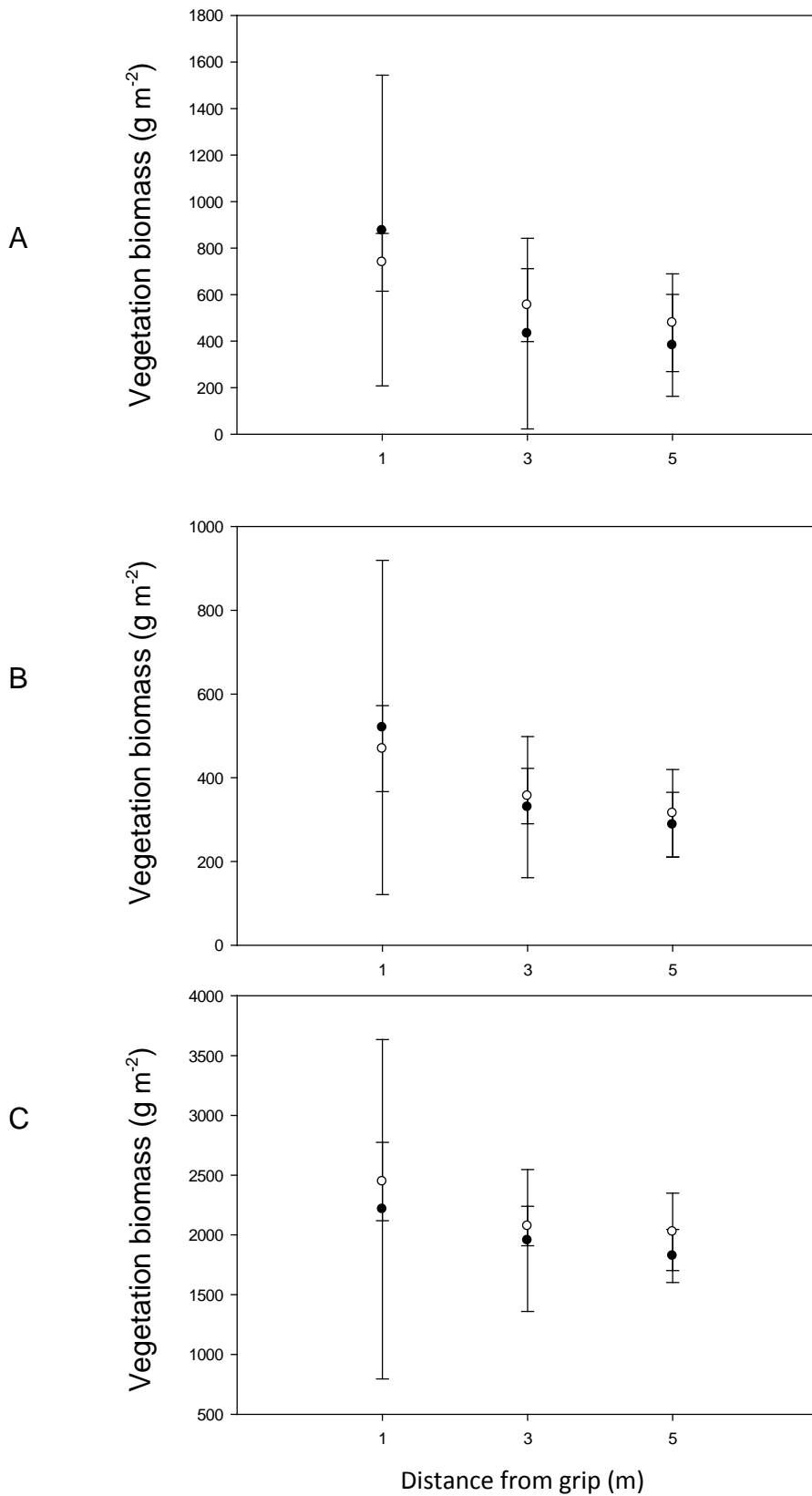


Figure 4.16. Scatterplots of mean vegetation biomass plotted against distance from the grip for Total Calluna (top), Calluna green shoots (middle) and all vegetation (bottom). Control plots are marked in black and treatment plots marked in white. Error bars indicate 95 % confidence intervals.

Using the estimated vegetation mass in Table 4.4., the LAI for vegetation species present in each plot was estimated using equations 3.6 & 3.7 derived in Chapter 3. As the LAI was based on the mass that had been estimated the results followed a similar pattern There were found to be no treatment differences between LAI for Total vegetation or individual species, Total vegetation (T = -1.13, P = 0.271), Green *Calluna* (T = -0.23, P = 0.816), *Eriophorum* (T = 0.08, P = 0.941), Moss and *Sphagnum* (T = -0.45, P = 0.655). There was no correlation between distance and the LAI for *Eriophorum*: control (r = 0.421, P = 0.298), treatment (r = 0.202, P = 0.575), Moss and *Sphagnum*: control (r = -0.351, P = 0.218), treatment (r = 0.076, P = 0.788), or Total vegetation: control (r = -0.336, P = 0.221), treatment (r = -0.489, P = 0.065). As with the mass, the green *Calluna* had a significant correlation in both the control (r = -0.542, P = 0.037) and treatment (r = -0.588, P = 0.021).

Table 4.5. Estimated Leaf area index for primary species at Newbiggin calculated using equations 3.6 and 3.7 and vegetation mass calculated from the vegetation survey.

Vegetation	Control	Treatment	T-Value	P
<i>Calluna</i> green	1.05	1.18	0.60	0.553
<i>Eriophorum</i>	0.39	0.38	-0.09	0.932
Mosses	0.72	0.74	0.42	0.677
Total vegetation	1.93	2.17	1.21	0.238

The leaf area index was used to attempt to predict the flux of the individual plots using equations 3.8 & 3.9 derived in Chapter 3, as shown in Figure 4.17. The flux for each measurement plot at 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR was estimated based on the LAI shown in Table 4.5. The predicted flux derived from LAI was compared against the modelled flux of the actual field measurements. They were found to correlate (r = 0.450, P = 0.013) as seen in Fig. 4.17. The LAI method of determining the flux provided an indication of the flux to be expected, but on average over estimated the modelled flux by 1.4  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and did not take account of a large amount of the variance.



## 4.5 Discussion

Overall grip blocking was found to have a very limited effect on both the water table and on the gas exchange. Significant differences in water table were only found within 0.5 m away from the edge of the grip. It was expected that the impact of the grip might be limited to the first few metres away from the grip, however such a limited impact was unexpected as the purpose of the grips was to lower the water table. However this does perhaps provide some explanation for why the practice of draining peatlands had not been felt to improve the agricultural productivity of the land and grip blocking was largely abandoned as a management practice.

Stewart & Lance (1991) measured the water table at another peatland in the North Pennines and only found changes in close proximity to the grip. They didn't find any significant mean lower water tables any further than 2.3 m away from the grip and at many grips the effect only extended between 0.3 – 1 m from the grip. It is likely that due to the ability of peaty soil to retain water, there is limited movement of water through the soil, therefore the creation of drains in peatland will not have the same effect as in well draining soils. Stewart & Lance (1991) suggested that some of the variation in the distance of the influence from the grip was due to the orientation of the grip, with limited effects detectable uphill from grips and higher effects measured downhill from a grip. This suggests that the impact of the grips may vary site to site and even within sites depending on the characteristics of the grip.

A similar limited impact of grips on vegetation was found by Bellamy *et al.* (2012) who also only detected an impact of the grip on vegetation 0.5 m away. They found that by 2.5 m away from the grip there was not a detectable impact upon the vegetation. They did not make intermediate measurements between 0.5 and 2.5 m, therefore it was not possible to determine the specific extent of the grip effect.

The fact that the effect of blocking the grips was so limited on the water table probably goes some way to explaining why there were no significant changes in the gas fluxes at the site. The closest gas flux measurements were made 1 m away from the edge of the grip, partly due to concern about the edge of the grip becoming unstable if flux chamber bases were dug in any closer. As a result, their position was

outside the measured impact area of the grip on water table levels. Prior to blocking taking place there was a weak correlation between the NEE and the distance from the grip, the NEE being higher further away from the grip as had been expected. However, in the second year, after blocking had occurred, neither the control or treatment grips had any correlation between NEE and distance from the grip. As the correlation in the first year was weak and there was no correlation in the second year, it is possible that this correlation is an artefact of limited observations over a short time period. As it has been shown that peatland NEE can change from year to year, it is also possible that the correlation was only apparent under certain environmental conditions and may not be apparent every year (Joiner 1999, Lafleur *et al.* 2001, Lafleur *et al.* 2003).

Komulainen *et al.* (1999) looked at the impact of drain blocking and showed an increase in water table depth and a subsequent reduction in CO<sub>2</sub> emissions. They found no effect of treatment on CO<sub>2</sub> assimilation overall, although in wetted plots where *Calluna vulgaris* was dying there was an increase in gross assimilation. The reduction in CO<sub>2</sub> emissions were put down to reduced rate of peat decomposition. However, their measurements were carried out for two years post blocking rather than the one year of measurements made in this study. It is therefore possible that the year immediately following restoration was too soon for some changes to be detectable. This was supported by Bellamy *et al.* (2012), who found vegetation changes at a field site with drains that had been blocked several years beforehand, but did not find a treatment effect for a site recently blocked.

A study looking at the impact of draining a peatland also indicated that changes may not occur in the immediate aftermath of blocking (Strack & Waddington 2007). They only found vegetation differences at the site two years after the draining had been carried out. In addition, they detected a reduction in methane in some areas during the first year post draining, but it was not until the following years that this reduction was seen across the entire site. As this suggests there was a lag in ecosystem response following drainage, it is reasonable to expect that there may be a similar lag in responses during restoration. Therefore detectable changes at the site may take a number of years to occur.

Strack & Zuback (2013) looking at a peatland 10 years after restoration found differences between pristine, drained and restored sites. Although the restored site did have higher water table levels than the drained site, the water table levels were still not raised as high as in the pristine site. The authors suggested that in periods of drought the drains may still have a draining effect on the surrounding soil. As shown in Fig. 4.8. in the year after blocking, even though the average water table was raised, the treatment grips still had outliers with lower water table depths closer to the grip, therefore it is possible that the grips do still influence the surrounding soil even once blocked.

Strack & Zuback (2013) also found that in spite of lower mean water tables at the restored site than the pristine site, the restored site was more productive, suggesting that water table was not the only factor affecting NEE. It has been found that restoration of peatlands can result in a greater number of species at the site (Poulin *et al.* 2013). The higher levels of NEE at the restored site could therefore be due to higher biodiversity at the site. The higher NEE at the restored site may be due to the restored peatland shifting to a growing ecosystem accumulating carbon as it recovers from the impacts of drainage. The pristine site may have already reached an equilibrium where inputs and losses of carbon are similar and it has ceased to accumulate. The growth of the restored site may therefore only last over a short period of time until it reaches the same stage as the pristine site.

It has been shown that peatland CH<sub>4</sub> fluxes are primarily driven by water table position (Yamulki *et al.* 2013, Koch *et al.* 2007). As changes in water table were only different 0.5 m from the grip in this study, that may be why differences in CH<sub>4</sub> fluxes were not detectable. However Strack & Zuback (2013) did not find any difference in CH<sub>4</sub> fluxes between drained and restored sites. They hypothesised that due to the drainage and past decomposition, the substrate was of poor quality and therefore there was limited potential for CH<sub>4</sub> flux under high water tables. As they found that the water table remained lower at the restored site than the pristine site, any new organic matter in the system may remain above the water table. In this study, the mean water table depth at the blocked grips was 7.5 cm below the soil surface. As measurements were only carried out during the first year after blocking,

it is likely that new inputs of organic matter remained predominantly above the water table, where aerobic decomposition may be more prevalent.

At both control and treatment plots the ER and CH<sub>4</sub> emissions both increased between the first and second years of measurements. For both gases, there was a significant increase in fluxes at the treatment plots, whereas the increase at control plots was not significant. For CH<sub>4</sub> this sort of change was hypothesised as the treatment was expected to increase CH<sub>4</sub> fluxes, however the opposite was true for ER, where the treatment was expected to reduce the ER flux. It is therefore possible that there is another factor at the treatment plots that has led to both fluxes increasing, or that initially after blocking, ER emissions can spike as water table rises.

There was also no significant impact on the vegetation between treatments at the site. This is to be expected due to the limited impact the grips appeared to have on the site and the evidence from previous studies that impacts on vegetation may take a number of years to develop (Bellamy *et al.* 2012, Strack & Waddington 2007). However there were some weak correlations with green *Calluna vulgaris* shoots and all vegetation. These correlations indicated that there was less *Calluna* green mass further away from a grip. Such a relationship would be expected as *Calluna vulgaris* prefers drier conditions and therefore the correlation may indicate a treatment effect (Bellamy *et al.* 2012).

The method used in Chapter 3 to estimate the NEE for a specified plot based on the vegetation surveyed there was applied to the measurement plots used in this chapter with mixed success. The vegetation survey was used to estimate the biomass and subsequently the values of LAI for each of the plots. These were then used to estimate the NEE at various levels of PAR. The estimated values provided a reasonable correlation with the values of NEE measured at the site. However, although there was a good correlation between the estimated measurements and field measurements, the vegetation survey method on average overestimated the flux by 1.4  $\mu\text{mol s}^{-1} \text{m}^{-2}$ . This indicates that the equations derived in Chapter 3 cannot be directly applied to separate field sites, as they are likely to give inaccurate flux levels.

It was found in Chapter 3 that the vegetation survey method of estimating the CO<sub>2</sub> flux correlated well with NEE, but not as well for respiration measurements. In Chapter 3 it was suggested that this was due to sources of CO<sub>2</sub> other than vegetation leaves, such as respiration from woody stems and organisms in the soil. It is possible that the overestimation of flux values could be due to increased CO<sub>2</sub> respiration in relation to vegetation at Newbiggin, compared to Whim in chapter three. Drainage has been linked with increased CO<sub>2</sub> emissions (Blodau *et al.* 2004, Komulainen *et al.* 1999). Therefore, even though it was not possible to identify significant differences in CO<sub>2</sub> fluxes between control and treatment grips or distance from grips, it is possible that the long term drainage of the site could have resulted in a general increase of CO<sub>2</sub> emissions across the site. This could reduce the NEE in comparison to undrained sites, explaining the overestimation of the vegetation survey method. In order to use the method at multiple sites it would be necessary to account for some of the causes of the CO<sub>2</sub> respiration variation observed, or carry out some measurements to derive suitable predictive equations for individual sites. However, with actual NEE measurements to calibrate the equations with, it should then be possible to predict the NEE at other locations at the site.

Measurements from this study and the literature suggest that the impact of grips varies between sites and even between individual grips within sites. The effectiveness of grip construction likely depends on the soil conditions at the site, gradient of the land and vegetation community. The frequency, size of the grip and orientation in relation to the gradient are also likely to have an effect on the influence of the grip. Although the grips studied in this chapter were relatively large, the site was a gently sloping hill and the grips ran directly down the hill. As a result, they may not intercept a significant amount of the water flow through the soil. This suggests that future work should include additional grips with different characteristics, so that there is a greater understanding of how different grips respond to restoration.

It is also indicated that there may be a delay between restoration work taking place and changes becoming detectable. As this study only took place during the first year after blocking it may be too soon for any changes to have occurred. Longer term

studies in the future would assist in the detection of changes that develop over longer time periods. While it has been suggested that restoration of drained peatlands could increase NEE above that of pristine peatlands, this is a consequence that may only be a temporary situation while the ecosystem grows. Therefore longer term studies would be important to determine the long term carbon balance of the ecosystem.

## 4.6 Conclusions

Extensive work is being conducted to block peatland drainage grips to restore peatlands and negate damaging impacts of drainage. However, it is unclear what effect this blocking will have on the water table and CO<sub>2</sub> and CH<sub>4</sub> fluxes. Measurements of water table, NEE, CO<sub>2</sub> respiration and CH<sub>4</sub> flux were carried out for a year before and a year after blocking of grips took place.

The grips were found to have a very limited effect on the water table prior to blocking, limited to 50 cm from the grip. Blocking the grips raised the water table within the first 50 cm, but had no effect beyond that. There was no impact of the grips on NEE, possibly due to the limited spatial effect of the grips. There was no difference between treatments for ER, however prior to the grips being blocked there was a weak correlation with distance, possibly suggesting that there were higher ER emissions closer to grips. CH<sub>4</sub> fluxes also showed no effect of the grip or blocking, however there was a significant increase in CH<sub>4</sub> and ER fluxes from the first to second years at the treatment grips.

There was no detectable effect of grip blocking on vegetation biomass. The method developed in Chapter 3 to estimate NEE from a vegetation survey was applied to measurements made in Chapter 4 and was found to overestimate the fluxes, suggesting that the method cannot be applied across sites without modification.

## **CHAPTER 5**

### **THE CARBON BALANCE OF AN UNDISTURBED OMBROTROPHIC PEATLAND**

## 5.1 Introduction

Peatland ecosystems are amongst the most important global stores of carbon, containing roughly 75 % of the amount of carbon present in the atmosphere (Parish 2008). Globally, although making up only 3 % of the global land surface, peatlands are estimated to contain around a third of the total soil carbon store (Charman 2002, Powlson 2005, Parish 2008, Wieder & Witt 2006). In the UK their carbon storage role is even more significant, as they contain 50.8 % of UK soil carbon stores while covering only 10.9 % of the land surface (Montanarella *et al.* 2006, Milne & Brown 1997). In the boreal zone, 79.5 % of carbon is stored within the peatland ecosystems (Parish *et al.* 2008).

This store of carbon within peatlands has accumulated over thousands of years since the last glaciation around 12,000 years ago (Clymo *et al.* 1998, Gorham *et al.* 2012). As ice sheets retreated around this time, it exposed biologically dormant land upon which peat was able to form, either through terrestrialization, the infilling of water by sediments, or paludification, where peat forms upon dry land (Anderson *et al.* 2003, Ruppel *et al.* 2013). Where climatic conditions were favourable, from this point peatlands accumulated vegetation and grew in height and breadth (Campbell *et al.* 2000, MacDonald *et al.* 2006, Parish *et al.* 2008). Over the long term peatlands typically accumulate 10 – 40 tonnes of carbon per km per year, which roughly equates to 0.5 – 1 mm vertical growth per year (Parish *et al.* 2008). These rates are very dependent upon the environmental conditions and may be slower or faster in arctic or tropical conditions and the rate within a single peatland may change from year to year.

This long term accumulation of carbon occurs when the rate of photosynthesis inputting CO<sub>2</sub> to the system exceeds the outputs of carbon emitted from the system through plant and invertebrate respiration, microbial activity and fluvial losses (Charman 2002). The rate at which carbon accumulates will depend on the difference between the inputs and outputs of carbon and can switch to a carbon losing system if the outputs exceed the inputs.

The rate of net primary production (NPP) is dependent upon the amount of photosynthesis and will control the amount of carbon input to the system. NPP has been estimated at levels between 100 – 400 g m<sup>-2</sup> yr<sup>-1</sup> (Moore *et al.* 2002, Blodau 2002). Measurements of CO<sub>2</sub> vary significantly between peatlands as it will be dependent upon the species composition at the site as well as the environmental conditions such as temperature, hydrology and the health of the ecosystem.

Moore *et al.* (2002) measured CO<sub>2</sub> fluxes at an ombrotrophic bog in Canada and found that it was capable of acting as both a sink and a source of CO<sub>2</sub>. The area went from being a sink of between 288 – 792 mg m<sup>-2</sup> h<sup>-1</sup> to a source of CO<sub>2</sub> during drier periods of between 36 – 468 mg m<sup>-2</sup> h<sup>-1</sup>. A further study of a Canadian peatland in Joiner (1999) found that there were significant differences in the carbon balance of the peatland between years. The peatland acted as a sink for CO<sub>2</sub> during one year, sequestering 91.6 g C m<sup>-2</sup>, however over the same period during a previous year the peatland acted as a source of CO<sub>2</sub>, releasing 30.8 g C m<sup>-2</sup>. It was assessed by the authors that the period during which the peatland was a source was due to an early thaw after a warm spring and a dry and warm autumn, which meant that CO<sub>2</sub> respiration was at a high level at times when the rate of photosynthesis was low. A third study into a Canadian peatland found that the site had a seasonal sink of 88 g C m<sup>-2</sup>, however these measurements were taken during the annual period of high productivity and there were indications at the beginning and end of the measurement period that the peatland was switching from a sink to a source (Suyker *et al.* 1997). This suggests that measurements over the full year will reduce the scale of the sink and even reveal the site to be a source of CO<sub>2</sub>.

Lafleur *et al.* (2001) measured CO<sub>2</sub> fluxes over a complete year in a Canadian peatland and found the site to be an annual sink of 67 g C m<sup>-2</sup> y<sup>-1</sup>. The study found a clear cycle between the summer where the NEE fluxes were approximately 116 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>, whereas during the winter months the peatland was on average a source of CO<sub>2</sub> of around 45 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>. Annual measurements at a peatland in Finland revealed it was an annual sink of 68 g m<sup>-2</sup> for CO<sub>2</sub>, however while during summer months the peatland acted as a sink of up to 9 g m<sup>-2</sup> d<sup>-1</sup>, during winter the peatland switched to a source of up to 2.5 g m<sup>-2</sup> d<sup>-1</sup> CO<sub>2</sub> (Aurela *et al.* 2002). This indicates that

estimates of annual peatland carbon balances should not be based solely upon measurements made over a single season as the peatland fluxes are likely to not be representative of the entire year.

In addition to seasonal variations in CO<sub>2</sub> fluxes, the annual carbon balance of a peatland may vary from year to year. Following on from measurements made in Lafleur *et al.* (2001) in Canada, it was found that the site went from being a strong annual sink of 260 g m<sup>-2</sup> y<sup>-1</sup> of CO<sub>2</sub> to only 34 g m<sup>-2</sup> y<sup>-1</sup> CO<sub>2</sub> the following year (Lafleur *et al.* 2003). The year of low CO<sub>2</sub> uptake coincided with dry summer conditions, which were assessed to be a primary cause for the smaller sink.

Measurements at a blanket bog in Ireland found that it was a sink of 49 and 61 g m<sup>-2</sup> y<sup>-1</sup> over consecutive years (Sottocornola & Kiely 2005). The site became a source of CO<sub>2</sub> during the winter months, however the sink over the summer was still sufficient for the site to be an annual sink. Similarly, Billet *et al.* (2004) found that over two years the annual carbon sink of a peatland in Scotland was 28 g m<sup>-2</sup> y<sup>-1</sup>.

Methane (CH<sub>4</sub>) is the second most important greenhouse gas in the atmosphere (IPCC 2007). Wetlands are responsible for 45 % of methane emissions and northern peatlands estimated to emit 9.8 % of wetland methane emissions (Segers 1998, Bartlett & Harriss 1993). They are therefore of interest as changes in their functioning could impact the methane concentration in the atmosphere, either by adding to methane emissions or reducing them.

Methane fluxes in peatlands are determined by the relationship between the production of methane by methanogens and the consumption of methane in the oxic region of the soil above the water table, a more detailed description of which is given in Chapter 1. As it is dependent on microbial activity the fluxes are particularly dependent on the water table, soil temperature, soil chemistry and vegetation type (Blodau 2002).

In chamber measurements of a Canadian peatland, Roulet *et al.* (1992) recorded fluxes of 21 mg m<sup>-2</sup> d<sup>-1</sup>. They found that the moisture of the soil was the key determining factor on emissions, followed by soil temperature. In another Canadian peatland, Edwards *et al.* (1994) measured fluxes of 16 mg m<sup>-2</sup> d<sup>-1</sup> over the course of

1 month during summer. During annual flux measurements of a Finnish peatland average fluxes of  $15 \text{ mg m}^{-2} \text{ d}^{-1}$  were recorded, with the highest measurements recorded during spring as the snow was melting (Hargreaves *et al.* 2001).

Suyker *et al.* (1996) measured methane fluxes in a Canadian peatland using eddy covariance, finding a range of fluxes from  $4.1 \text{ mg m}^{-2} \text{ h}^{-1}$  to  $19.5 \text{ mg m}^{-2} \text{ h}^{-1}$ . They found that water table and temperature were responsible for 68 – 94 % of the variability in fluxes.

In the UK average methane flux measurements of  $15 \text{ mg m}^{-2} \text{ h}^{-1}$  have been recorded at peatland sites (Hargreaves & Fowler 1998). Beverland *et al.* (1996) recorded  $\text{CH}_4$  fluxes at a site in Scotland of between  $-70$  to  $+110 \text{ } \mu\text{mol m}^{-2} \text{ h}^{-1}$  and a mean flux  $23 \text{ } \mu\text{mol m}^{-2} \text{ h}^{-1}$ . A synthesis of  $\text{CH}_4$  fluxes at numerous sites with organic soils in the UK found mean fluxes ranging from  $-0.3$  to  $27.4 \text{ nmol m}^{-2} \text{ s}^{-1}$  (Levy *et al.* 2012).

While fluxes of  $\text{CO}_2$  and  $\text{CH}_4$  between the land surface and atmosphere are the most significant pathways that carbon is input or lost from a peatland, there can also be a significant loss of carbon through fluvial fluxes. Carbon can be lost in the fluvial fluxes as dissolved organic carbon (DOC), particulate organic carbon (POC), dissolved inorganic carbon (DIC) and dissolved  $\text{CO}_2$  and  $\text{CH}_4$ . Often only  $\text{CO}_2$  and/or  $\text{CH}_4$  fluxes between the land and atmosphere are measured, however studies in the UK have indicated that when fluvial fluxes are accounted for peatlands may be a smaller sink or even a source (Billett *et al.* 2004, Worrall *et al.* 2003).

Worrall *et al.* (2003) combined land atmosphere fluxes of  $\text{CO}_2$  and  $\text{CH}_4$  with the losses of carbon from DOC and POC. Once all of these components had been taken into account, they determined that the peatland was still acting as a sink of  $15.4 \text{ g m}^{-2} \text{ y}^{-1}$ , which was smaller than previous estimates for the site. Waddington & Roulet (2000) measured the carbon balance of a Swedish peatland and found a sink of  $-2.0 \text{ g C m}^{-2} \text{ y}^{-1}$  in the first year, but lost  $7.6 \text{ g C m}^{-2} \text{ y}^{-1}$  the following year. Over the two years they found that DOC and DIC accounted for losses of  $4.2$  and  $6.7 \text{ g C m}^{-2} \text{ y}^{-1}$  from the ecosystem respectively, indicating the importance of taking into account the fluvial fluxes as they were sufficient to alter the flux of the ecosystem from a sink to a source.

Additionally, there is evidence that fluvial fluxes, especially DOC are increasing and therefore in the future fluvial losses of carbon may become even more significant (Evans *et al.* 2005, Freeman *et al.* 2001, Worrall *et al.* 2003, Worrall *et al.* 2004). A number of theories for this increase have been proposed, including lowered water tables, increased temperature, increased CO<sub>2</sub> concentrations, altered discharge rates, recovery from acidification and an enzymic latch mechanism (Evans *et al.* 2002, Pastor *et al.* 2003, Freeman *et al.* 2001a, Freeman *et al.* 2004, Freeman *et al.* 2001b).

Many peatlands in the UK are no longer considered to be in a pristine state as they have been impacted by management practices such as drainage, burning or grazing or have been subjected to pollution or changes in climate. Peatlands that are relatively unaffected by human activity are generally found in remote areas. As concerns have been raised regarding carbon emissions these largely unmanaged peatlands have been assumed to be a healthy store of carbon and possibly even a sink for carbon. Even though many are not subjected to management practices it is possible that due to pollution and changing climate they may have experienced changes that have gone unnoticed and are not behaving in their natural state as expected. As peatlands can act as both a source and sink for CO<sub>2</sub> and CH<sub>4</sub>, changes in their functioning have the ability to impact climate change.

However, there has been limited study of the sites in the UK. As many are remote sites it increases the difficulty of obtaining good quality continuous measurements over extended periods. As a result, for many of the peatland areas within the UK it is not known what their carbon state is, even when considered to be in “pristine” condition.

## 5.2 Aims

This chapter aims to use continuous measurements of CO<sub>2</sub> exchange along with regular chamber measurements of CH<sub>4</sub> exchange in order to estimate the annual terrestrial budget of an undisturbed bog in the UK for CO<sub>2</sub> and CH<sub>4</sub> and the overall carbon budget. This will indicate whether the site is acting as a sink and store of carbon as believed, or whether even peatlands in the UK that have been assessed to be undamaged and therefore stores of carbon are in fact losing carbon. As the site is not subjected to management practices and is located in a remote area of the country with limited human impacts it is expected that the ecosystem functioning will be undisturbed. It is therefore hypothesised that the site will be an annual sink for CO<sub>2</sub> and an annual source of CH<sub>4</sub>. As the site is still in a pristine state, it is expected that the inputs of carbon through CO<sub>2</sub> will exceed the losses of carbon through CH<sub>4</sub>.

## 5.3 Methods

### 5.3.1 Field site

Field measurements were carried out at the Royal Society for the Protection of Birds (RSPB) reserve at Forsinard Flows, British National Grid reference NC852441. The site is located within The Flow Country of Caithness and Sutherland in northern Scotland, which contains the largest stretch of continuous Blanket Bog in Europe (NCC 1987). As the area is in the extreme north of the UK mainland it is one of the remotest parts of the UK, with no significant cities or industry nearby. The bogs in Caithness and Sutherland lie on ground between 10 – 450 metres in altitude and originally covered 401,375 ha. The peatlands cover predominantly flat areas of land containing open pools of water, spongy ridges, hollows and hummocks of vegetation and *Sphagnum* “lawns” (Stroud *et al.* 1988).

The peatlands in the flows contain many of the species found in peatlands across the UK such as *Sphagnum* spp, *Eriophorum angustifolium*, *Calluna vulgaris* and *Erica tetralix*. The flows are an important habitat for a number of breeding bird species, including dunlin, green shank, golden plover, arctic skewer, greylag geese and wood sandpiper. The area also supports raptor populations including hen harriers, golden eagles, merlin and short eared owls, some of which are endangered within the UK (Stroud *et al.* 1988). The peatlands are also inhabited by populations of moths, beetles, amphibians and adders.

Although the peatlands in The Flow Country have not been subjected to the same pressures as some of the peatlands in less remote areas, many areas have previously been burned, drained and used for forestry plantations. However, in recent years there has been a shift towards felling forested areas and filling in drains to allow the bog to regenerate. Due to the low productivity of the land, there has been a limited amount of agricultural grazing, however there are significant numbers of wild deer present in the area.

The area used for the field study had not been subjected to any previous management practices, however it was adjacent to a felled forestry plantation. As seen in Fig. 5.1.

the field site is on gently sloping ground at altitude between 200 – 220 metres. The mean annual temperature for the Flow Country is between 7.5 – 8.0 °C and annual precipitation between 650 – 1000 mm. The vegetation at the site is dominated by *Sphagnum* mosses and dwarf shrubs such as *Calluna* and *Eriophorum*, and has numerous open pools of water.



Figure 5.1. Photograph of the field site taken from the east. The flat area beyond the nearest gully was used for measurements. The flux tower is situated in the centre of the photograph.

### 5.3.2 Methane fluxes

Methane fluxes were made using the closed chamber method described in Chapter 2. There were 20 chamber bases installed permanently around the flux tower area to take into account different vegetation and topography types present at the site. Measurements were made in two batches, 10 plots at a time, one following the other, taking five air samples over an 80 minute enclosure period. Measurements were made on four occasions between August 2010 – October 2011 approximately every 2

– 3 months, however there were periods where due to the site location it was not possible to reach it because of flooding, heavy snowfall or deer stalking. Gas samples were analysed on the gas chromatograph (GC) within 48 hours of having been collected in the field.

For the period that measurements were made a CR10X data logger (Campbell Scientific) was used to record average environmental variables for one minute intervals. Air temperature was monitored using a 107 thermistor probe located within a radiation shield (Campbell Scientific) and soil temperature was monitored using a 105 thermocouple probe (Campbell Scientific). These sensors were located in the centre of the experimental area and the air temperature sensor positioned approximately one metre above the ground. The time at which air samples were extracted from the headspace was recorded and the average data logger measurement for the entire enclosure time was used to relate the flux measurements to the environmental variables at the site.

### **5.3.3 CO<sub>2</sub> fluxes**

Gas fluxes between the land and atmosphere are often measured using a flux chamber method, partly due to their relative simplicity and cheap cost (Norman *et al.* 1997, Pumpanen *et al.* 2004, Janssens *et al.* 2001). Many components for constructing flux chambers are not purpose built, often with only the air sampling and measurement technique involving specialised component. As a result it can be affordable to construct a significant number of chambers, which allows measurement at numerous plots. There are three main flux chamber methods frequently used to measure gas fluxes; closed-static, dynamic-closed and open chambers (Norman *et al.* 1997).

Closed-static chambers consist of a chamber headspace which is left in place for a period of time, while regular gas samples are removed. These samples are then analysed in a laboratory to determine the gas concentrations within the sample and subsequently the flux rate. Dynamic-closed chambers involve the same closed headspace as in a static chamber, however air is circulated between the chamber and

a connected gas analyser, which continuously measures the gas concentration and derives the flux rate. Open-chambers pump atmospheric air into a chamber headspace, while at the same time removing air from the chamber. The difference in the gas concentration within the atmospheric and chamber air is measured and combined with the flow rate to determine the flux (Norman *et al.* 1997).

Closed-static methods require very little equipment to present at the measurement site and as a result it is practical to sample numerous chambers covering a large spatial area. However, this method requires a significant amount of manual labour and as a result there may be a limited number of measurements made for each measurement plot over time (Savage & Davidson 2003). Dynamic chambers require an analyser to make measurements at the plot, which allows for a large number of measurements over time per plot and automated measurements. However, the cost of portable gas analysers can be prohibitive and limit the number of plots that measurements can be made at. The number of plots measured by a single analyser can be increased by the use of a multiplexer, which switches the flow of air to the analyser between multiple plots (CTCD 2007).

A disadvantage of chamber methods is the potential impact of equipment upon the fluxes. Establishing a chamber headspace in which to measure the gas flux creates an area which may experience atypical conditions due to increased gas concentrations, pressure changes and altered temperature. Closed-static and dynamic-static methods both result in increased gas concentrations within the chamber headspace, which can result in the flux rate decreasing over time (Kroon *et al.* 2008). In addition, installing the chamber can result in disturbance to the vegetation and soil, which may influence the fluxes (Heinemeyer *et al.* 2011).

When attempting to measure fluxes at a landscape scale eddy covariance techniques are often used to provide more spatially representative flux values than flux chambers (Waddington & Roulet 2000, Lafleur *et al.* 2003). Atmospheric air contains turbulent air which moves up and down in eddies. Eddy covariance samples a fixed point of air to measure the concentration of gas and vertical velocity at that point. The samples are then analysed to determine an average of the fluctuations over

a specified time period. This gives the net amount of a gas that moved vertically at a specific height (Aubinet *et al.* 2012, Baldocchi 2003).

Eddy covariance is more suitable for ecosystem fluxes than flux chambers for a number of reasons. Eddy covariance can be scaled up to measure a large area, rather than the small flux chamber area. The technique does not have a significant impact on soil and vegetation as chambers can have, as it does not require the measurement area to be enclosed. It is possible to calculate fluxes over varying periods such as hourly or annually and measurements can be maintained for years. This allows flux measurements to be made over significant time periods and to investigate long term trends and the responses of fluxes to environmental variables (Baldocchi 2003).

While eddy covariance has significant advantages over chamber measurements, there are some drawbacks that may make the method unsuitable in some cases. The principle of eddy covariance requires certain assumptions to apply. Ideally the measurement area should be flat, have homogenous vegetation cover, steady environmental conditions and no advection (Baldocchi 2003). When conditions are calm and windless, this may result in systematic errors as the criteria are not met (Goulden *et al.* 1996, Reth *et al.* 2005). Outputs from eddy covariance may therefore contain periods of missing data. The fluxes for these periods can often be estimated using basic interpolation or using environmental variables known to drive fluxes to calculate the flux (Moncrieff *et al.* 1996, Baldochhi 2003).

As eddy covariance measures a spatially averaged flux, it does not allow the flux for specific areas or vegetation types to be investigated or compared. In addition, eddy covariance measurements give the NEE flux for the site, but cannot be used to directly measure the ecosystem respiration. The night time values of NEE can be used to determine what the ecosystem respiration of the site will be, typically in relation to temperature. However it has been suggested that this can result in biased results due to seasonal effects (Reichstein *et al.* 2005). The use of chambers in conjunction with eddy covariance measures has been suggested as an approach to resolve these issues (Waddington & Roulet 2000).

The Centre for Ecology & Hydrology (CEH) has set up a network of UK peatland field sites as part of the Carbon Catchments project, including Forsinard, to measure long term carbon fluxes at the sites. The site at Forsinard was established in 2008 and an eddy covariance flux tower (shown in Fig. 5.2) was set up prior to the start of this study to measure NEE. The eddy covariance data was collected and processed by Peter Levy at CEH.

The flux tower was powered by a bank of 12 V DC lead acid batteries which were charged from a combination of six solar panels and a wind turbine. The CO<sub>2</sub> concentration was measured using an LI-7500 open path CO<sub>2</sub> / H<sub>2</sub>O analyser (Li-Cor Environmental) and three dimensional measurements of wind speed and direction made using a sonic anemometer. PAR was measured using a quantum sensor (SKYE instruments). Measurements from the equipment were recorded on CR23X and CR3000 data loggers (Campbell Scientific) and averaged over a 30 minute period to give mean values for environmental conditions, fluxes and total accumulated CO<sub>2</sub> for the period. Data was remotely downloaded from the loggers on a daily basis using a GSM connection.



Figure 5.2. Photograph of the CO<sub>2</sub> flux tower with key components indicated.

## **5.4 Results**

### **5.4.1 Environmental conditions**

Environmental variables were measured at the site from April 2008 through to October 2010. There was a significant gap in data between January – April 2009 as there was a lack of power due to the wind turbine not operating, which prevented automated measurements taking place. The temperatures during the period of measurements ranged from a maximum of 26.2 ° C to a minimum of -8.8 ° C. As seen in Fig. 5.3 there was a seasonal pattern in the mean monthly temperatures, which ranged from a minimum of -0.1 ° C in February 2010 to a maximum of 8.9 ° C in July 2009. The water table level varied between 18.2 cm deep and 6.1 cm above the soil at the site. However, the mean water table depth was only 1.4 cm below the soil during the measurement period.

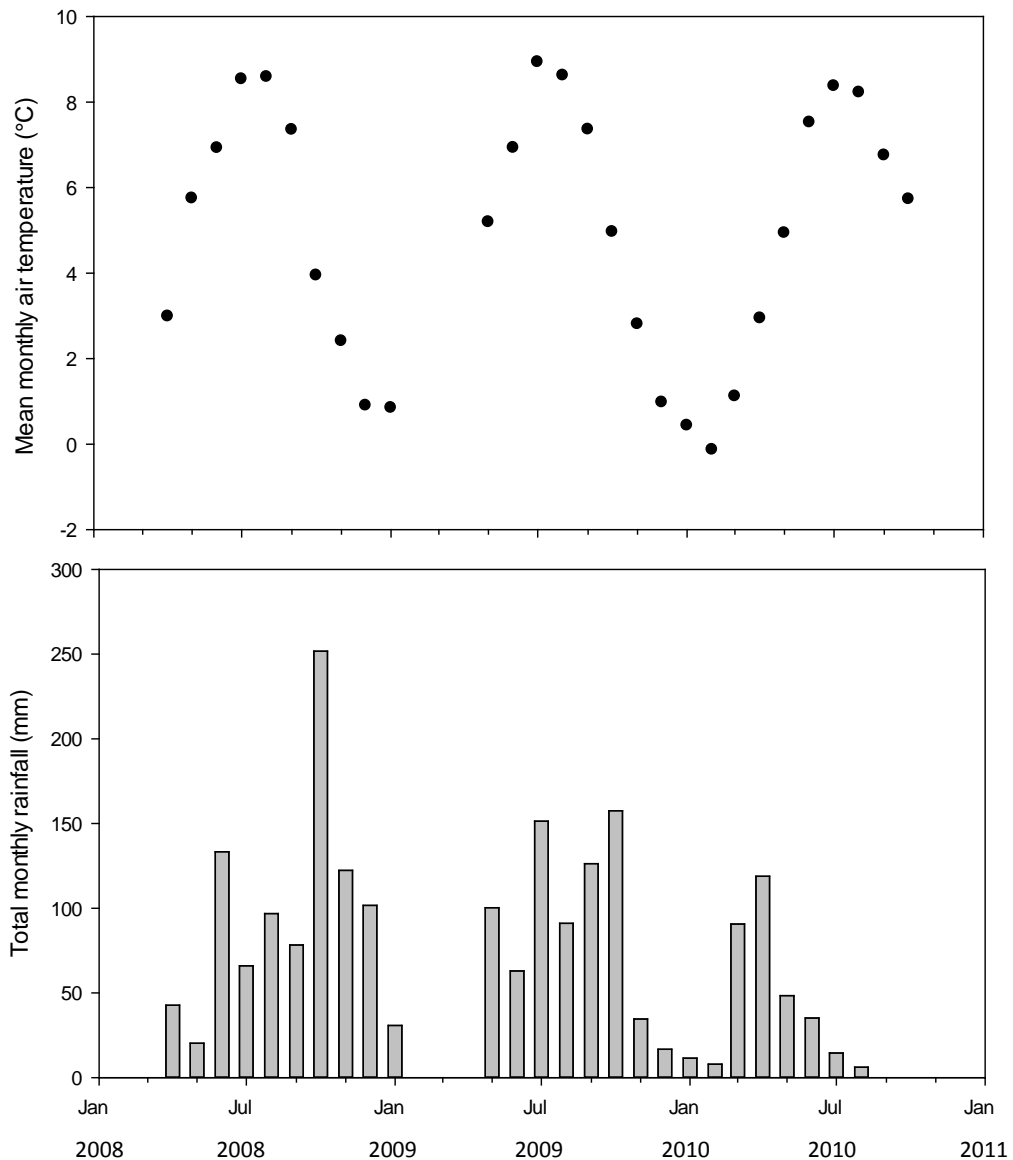


Figure 5.3. Mean monthly air temperature and total monthly rainfall for the measurement period between April 2008 – October 2010.

### 5.4.2 Methane fluxes

There were a wide range of CH<sub>4</sub> fluxes measured during visits to the site from, -0.26 to 95.34 nmol m<sup>-2</sup> s<sup>-1</sup>. CH<sub>4</sub> emissions are highly dependent upon water table levels, however automated measurements of water table depth were not available during the period that CH<sub>4</sub> measurements were made. As a result, water table depth could not be used when estimating the annual emissions of CH<sub>4</sub> from individual plots at the

site. As seen in Fig. 5.4, there was a correlation between monitored air temperature and the manual water table depth measured at individual plots when CH<sub>4</sub> was measured at the site. Air temperature was therefore felt to be a reasonable substitute for water table to predict CH<sub>4</sub> fluxes and calculate the annual gas flux.

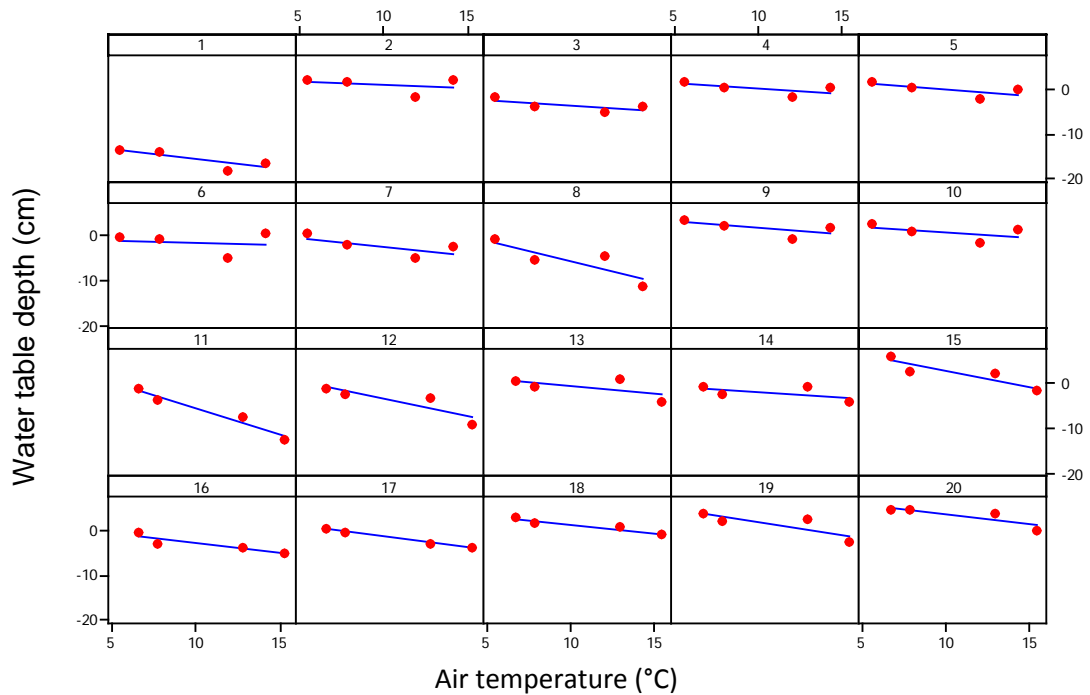


Figure. 5.4. The relationship between manually measured water table depth and air temperature at the 20 individual measurement plots at Forsinard when measurements were made at the site.

The relationships between air temperature and CH<sub>4</sub> flux for each individual plot are shown in Fig. 5.5. A linear regression was used for each individual plot to determine the relationship between the CH<sub>4</sub> flux and air temperature. The derived equation was used with the continuous air temperature measurements recorded at the site to estimate the mean CH<sub>4</sub> fluxes per half hour for each individual plot between April 2008 – October 2010. The mean flux value for all 20 of the plots was used to determine the estimated site wide flux.

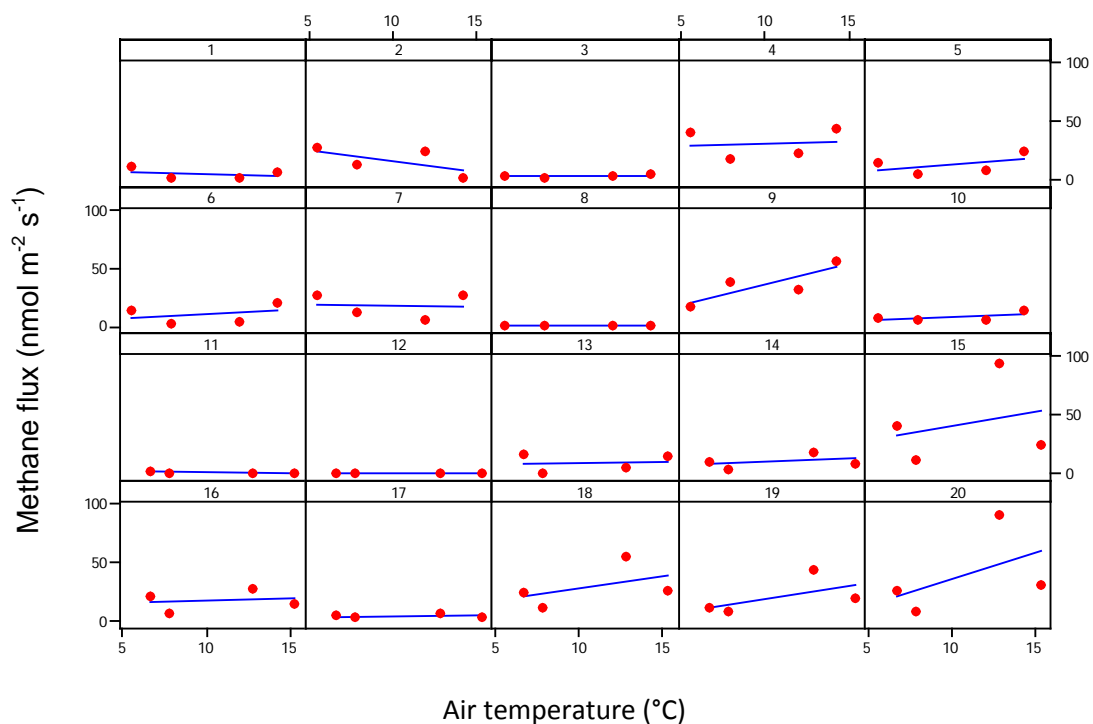


Figure 5.5. Plotted relationships between measured methane fluxes and recorded air temperature during enclosure periods for the 20 individual measurement plots.

Throughout the measurement period it was calculated that there was a continuous emission of methane to the atmosphere as seen in Fig. 5.6. Although there were individual plots that showed some net methane oxidation at times during the year, this was exceeded by the methane emissions from other plots. The calculated rate of methane emission varied seasonally, with highest daily mean site rates of  $16.78 \text{ nmol m}^{-2} \text{ s}^{-1}$  during the summer months when average temperatures were high and a reduced daily mean site rate as low as  $1.58 \text{ nmol m}^{-2} \text{ s}^{-1}$  during the winter months.

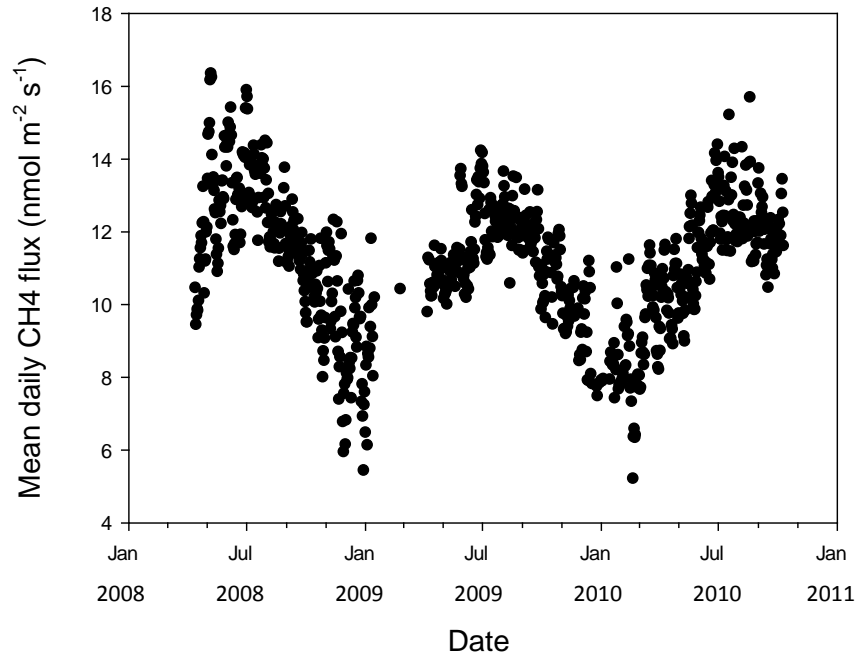


Figure 5.6. The site wide mean daily methane flux for the measurement period estimated from chamber flux measurements.

For the period where power failure prevented the monitoring equipment functioning, there were no air temperature measurements for the site which could be used to calculate the CH<sub>4</sub> fluxes during that period. The nearest Meteorological Office weather station to the Forsinard field site is at Wick Airport, 32 miles to the east. Data from the months the field site equipment was functioning were compared to the data from the Wick weather station during this period and found to have a strong correlation as seen in Fig. 5.7 (0.990,  $P < 0.001$ ). This relationship was used to estimate the mean monthly temperature at Forsinard during the periods of missing data. The mean monthly Forsinard temperature was calculated using the following equation:

$$\text{Forsinard mean monthly temp} = - 2.08 + 0.782 \times \text{Wick mean monthly temp.} \quad (5.1)$$

The estimated mean monthly temperature at Forsinard during periods of missing data was then used to calculate the daily methane emission during this period and taken into account when calculating the cumulative amount of methane exchanged between the land and the atmosphere.

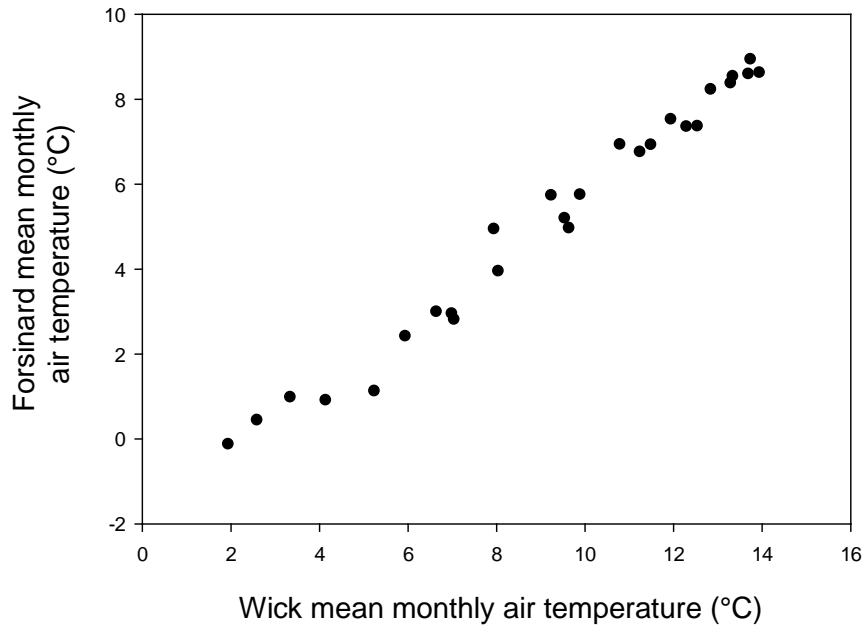


Figure 5.7. Plot of the mean monthly air temperatures at Wick and Forsinard during the months data were available at Forsinard.

As seen in Table 5.1. during summer months, the monthly emission of methane was calculated to be around 30 – 45 mmol m<sup>-2</sup>. In comparison during winter months monthly emissions of methane fell to between 20 – 25 mmol m<sup>-2</sup> for most months, with the lowest monthly emissions falling to less than 5 mmol m<sup>-2</sup>. While the rate varied throughout the year, site was estimated to be a source of methane all year round, leading to a constant increase in the cumulative amount of methane released as seen in Fig. 5.8.

Table 5.1. Emissions of methane per month during the measurement period including total quantity emitted each month as well as maximum and minimum daily emissions. Note that April 2008 and October 2010 do not include full monthly data due to the start and end points of measurements.

Month	Total emission (mmol m <sup>-2</sup> )	Maximum daily emission (μmol m <sup>-2</sup> )	Minimum daily emission (μmol m <sup>-2</sup> )
April 2008	15.65	26.11	15.31
May 2008	39.21	34.95	19.45
June 2008	38.32	32.30	21.17
July 2008	41.13	33.65	21.88
August 2008	35.03	29.50	20.25
September 2008	30.81	25.09	17.94
October 2008	25.93	22.05	11.21
November 2008	24.44	23.52	5.37
December 2008	18.68	19.12	3.92
January 2009	6.59	22.04	5.89
February 2009	0.09	18.10	18.10
March 2009	4.65	19.79	17.20
April 2009	9.22	21.49	16.30
May 2009	27.69	27.48	16.90
June 2009	29.19	28.91	17.42
July 2009	28.47	28.75	20.41
August 2009	28.46	27.29	18.53
September 2009	27.73	25.88	19.10
October 2009	18.81	22.71	15.34
November 2009	10.09	18.70	12.49
December 2009	5.36	20.30	9.74
January 2010	5.74	19.79	9.56
February 2010	8.00	20.41	3.28
March 2010	23.46	21.51	10.24
April 2010	24.97	22.01	11.80
May 2010	27.84	25.40	14.02
June 2010	32.99	28.70	18.83
July 2010	36.69	31.72	21.04
August 2010	30.77	33.09	20.22
September 2010	31.96	27.54	18.21
October 2010	11.73	26.70	21.35

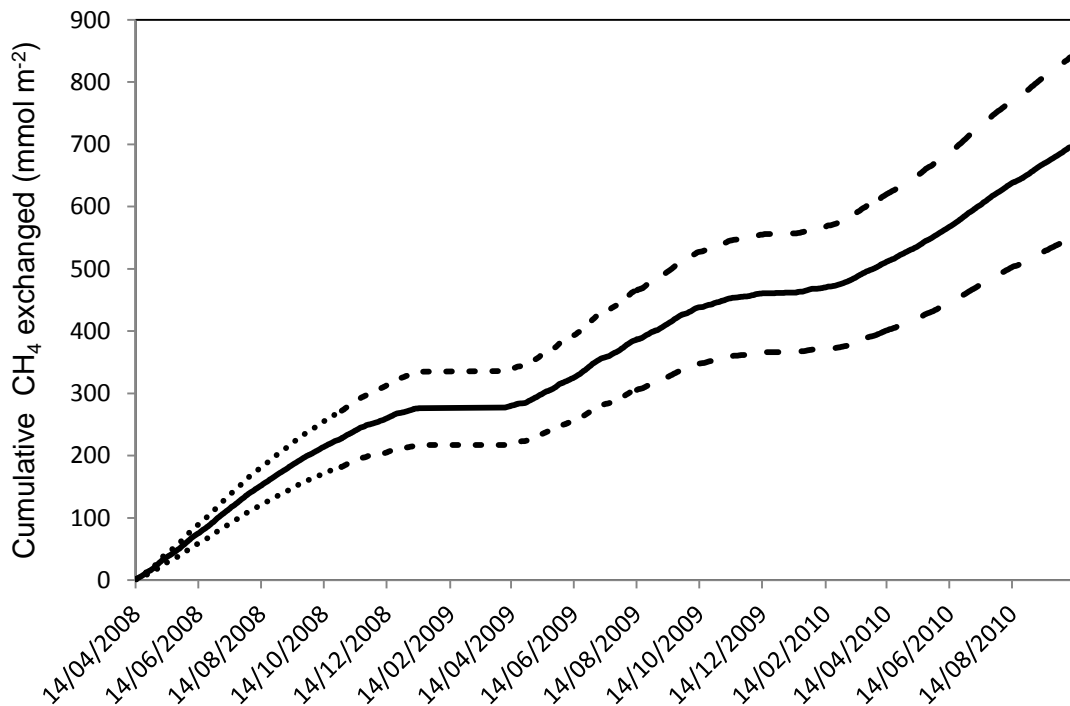


Figure 5.8. The estimated cumulative methane emitted from the site during the measurement period based on the estimated methane fluxes. The solid line shows the estimated cumulative CH<sub>4</sub> flux and dashed lines indicate the standard error of the measurements.

In the first full year of measurements from May 2008 – April 2009 the area released 274.10 mmol m<sup>-2</sup> of methane to the atmosphere in total. The following year from May 2009 – April 2010 the total CH<sub>4</sub> released was slightly lower at 237.97 mmol m<sup>-2</sup>. There were only five months of complete measurements from the third year, between May – September 2010, therefore a third full year cannot be compared. However, during the same period from the previous two years the total released was 184.50 mmol m<sup>-2</sup> (year 1) and 141.54 mmol m<sup>-2</sup> (year 2), while the same period in the third year released 160.25 mmol m<sup>-2</sup>. The annual CH<sub>4</sub> budget is therefore estimated to be 256.04 ± 54.35 mmol m<sup>-2</sup>.

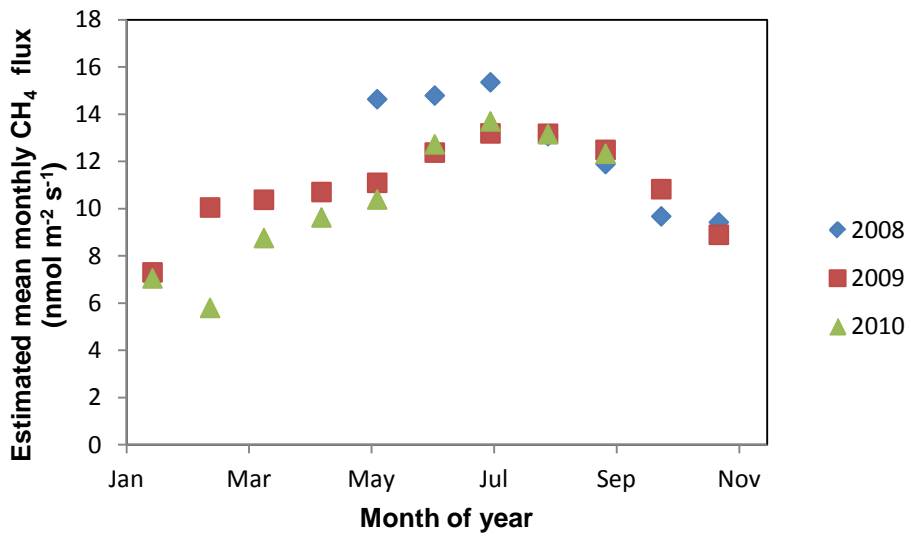


Figure 5.9. A scatterplot showing the calculated monthly site wide methane emissions between 2008 – 2010.

Fig. 5.9. shows there is a broadly seasonal relationship of CH<sub>4</sub> emissions over the years that measurements were made, although during periods of 2008 and 2010 there are some outlying emissions estimates. As these CH<sub>4</sub> estimates are based on air temperature alone at the site, these outlying points may be due to abnormally warm or cold months. The variation in the monthly CH<sub>4</sub> fluxes between years seen in Fig. 5.9. explains the variation in the annual levels of CH<sub>4</sub> released during different years.

### 5.4.3 NEE measurements

Fluxes of CO<sub>2</sub> during the measurement period ranged from a maximum uptake of 8.77  $\mu\text{mol m}^{-2} \text{s}^{-1}$  to a maximum emission of 7.15  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . There was a seasonal pattern to the mean daily fluxes as seen in Fig. 5.10, with average flux from the atmosphere to soil during the summer months and a release of CO<sub>2</sub> into the atmosphere during the winter months when solar radiation was lower.

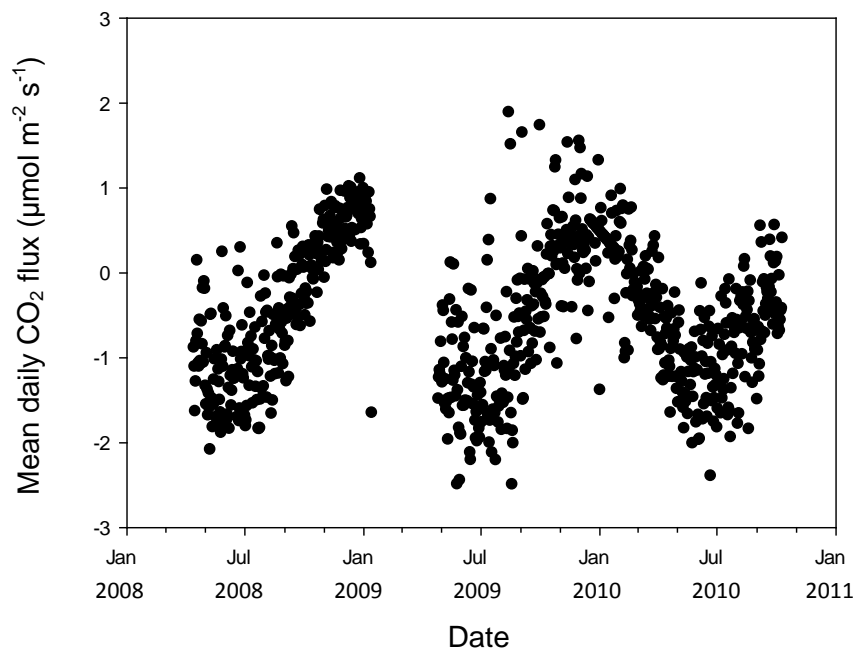


Figure 5.10. The mean daily CO<sub>2</sub> flux during the measurement period plotted against time.

When calculating the total amount of CO<sub>2</sub> accumulated during the measurement period it was necessary to make an estimate of the CO<sub>2</sub> fluxes during the period when the flux tower was not operational. The mean daily CO<sub>2</sub> flux was closely related to the mean daily PAR as seen in Fig. 5.11. However there were no measurements of solar radiation made at the site or in the vicinity that could be used

to estimate the mean solar radiation at the site, as with CH<sub>4</sub>. Therefore, the 30 days preceding and following the period of missing data were taken and a linear regression of the period used to estimate the missing values and estimate the mean daily CO<sub>2</sub> flux during this period.

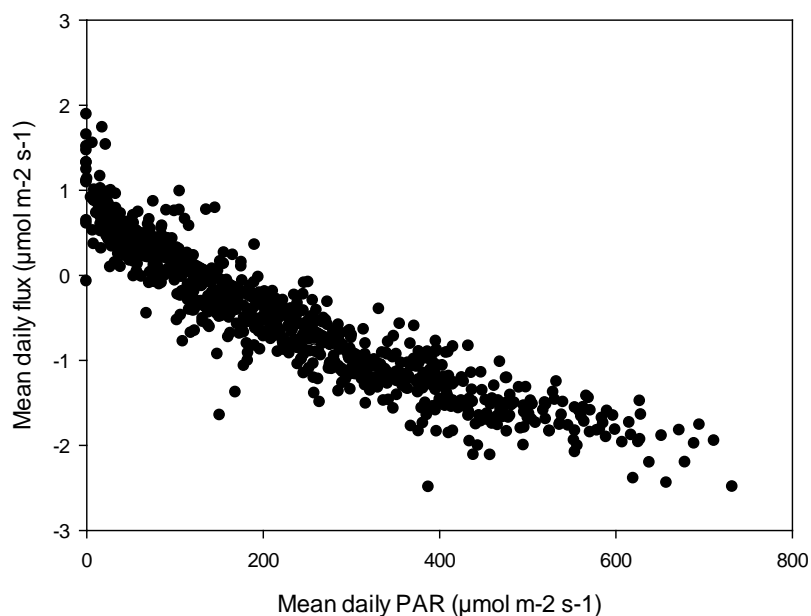


Figure 5.11. Mean daily CO<sub>2</sub> flux plotted against mean daily PAR between April 2008 – October 2010.

The daily quantity of CO<sub>2</sub> being exchanged between the land and atmosphere followed the same pattern as seen for the mean daily CO<sub>2</sub> flux. As seen in Table 5.2. during summer months the peatland acted as a sink for CO<sub>2</sub> of up to 3.56 mol m<sup>-2</sup> per month, while in the winter the peatland released up to 1.90 mol m<sup>-2</sup> in a month.

Table 5.2. The monthly total uptake for CO<sub>2</sub> and the highest and lowest daily amounts of CO<sub>2</sub> exchanged during those months.

Month	Total uptake (mol m <sup>-2</sup> )	High daily exchange (mol m <sup>-2</sup> )	Low daily exchange (mol m <sup>-2</sup> )
May 2008	-3.42	0.02	-0.18
June 2008	-2.90	0.03	-0.16
July 2008	-3.16	-0.01	-0.16
August 2008	-1.97	0.03	-0.14
September 2008	-0.74	0.05	-0.11
October 2008	0.25	0.06	-0.05
November 2008	1.29	0.08	-0.01
December 2008	1.90	0.10	0.03
January 2009	0.89	0.09	-0.14
February 2009	-0.29	0.01	-0.03
March 2009	-1.44	-0.03	-0.06
April 2009	-2.55	-0.07	-0.13
May 2009	-3.19	0.01	-0.22
June 2009	-3.56	-0.02	-0.19
July 2009	-3.24	0.07	-0.19
August 2009	-2.58	0.16	-0.22
September 2009	-1.10	0.14	-0.13
October 2009	0.32	0.15	-0.09
November 2009	0.82	0.13	-0.07
December 2009	1.43	0.13	-0.04
January 2010	0.82	0.08	-0.12
February 2010	0.25	0.08	-0.09
March 2010	-0.65	0.04	-0.06
April 2010	-2.11	0.01	-0.14
May 2010	-3.31	-0.04	-0.17
June 2010	-3.12	-0.01	-0.21
July 2010	-2.80	-0.01	-0.17
August 2010	-1.84	0.01	-0.16
September 2010	-0.93	0.05	-0.13

As seen in Fig. 5.12. this variation of the site between a sink and source for CO<sub>2</sub> meant that during the spring and summer months the bog removed CO<sub>2</sub> from the atmosphere, while in the autumn and winter months the bog became a source of CO<sub>2</sub>. During the measurement period the site overall the uptake of CO<sub>2</sub> exceeded the emissions and the site was a sink for CO<sub>2</sub> and a total of 38.4 mol m<sup>-2</sup> was taken up.

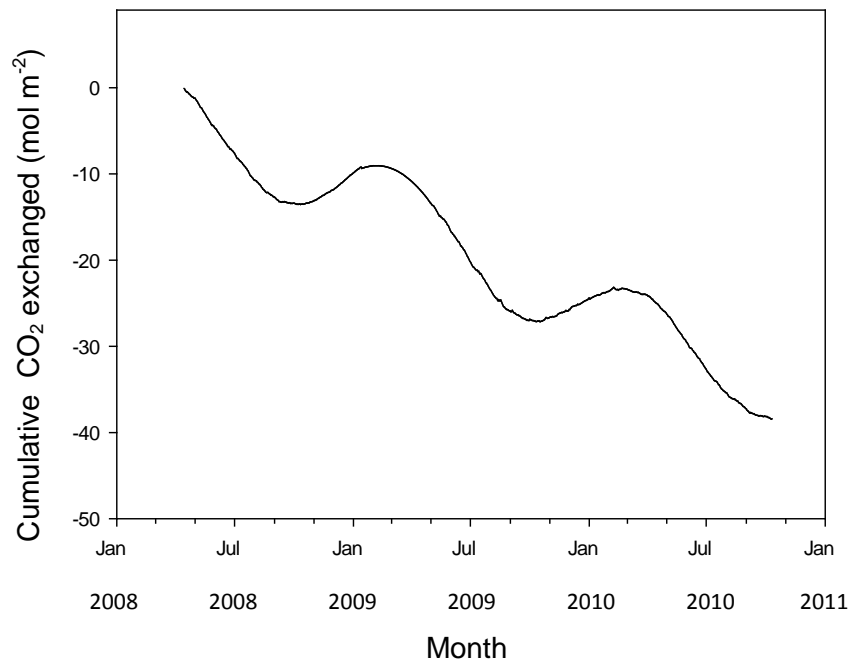


Figure 5.12. The cumulative CO<sub>2</sub> exchange measured by eddy covariance during the measurement period.

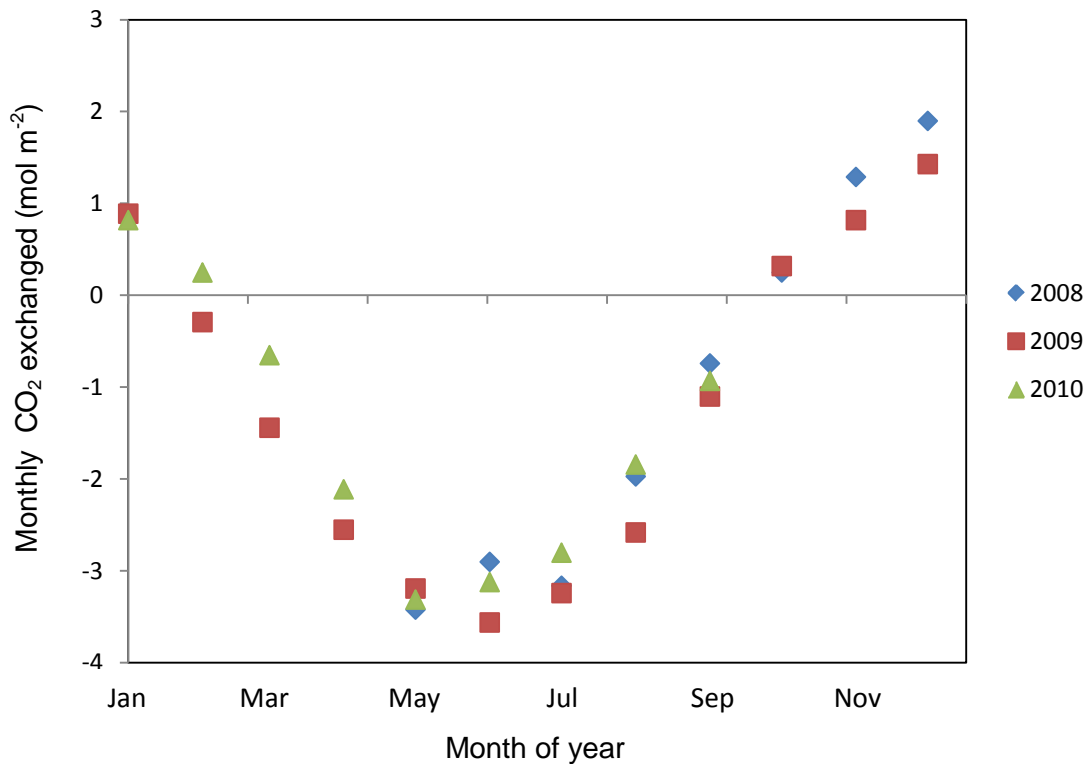


Figure 5.13. The monthly quantity of CO<sub>2</sub> exchanged by year. The first full measurements in 2008 started in May and the final available measurements in 2010 were in September.

Fig. 5.13. shows the seasonal relationship for the CO<sub>2</sub> flux over the course of multiple years. While the NEE was broadly similar for the same months across different years, there were noticeable variations in the quantity of CO<sub>2</sub> exchanged between years. However during the measurement period the ecosystem was consistently a CO<sub>2</sub> sink between the months March – September and a source between October – January.

In the first full year of measurements from May 2008 – April 2009 the area accumulated 12.1 mol m<sup>-2</sup>. The following year from May 2009 – April 2010 the total accumulation was slightly higher at 12.8 mol m<sup>-2</sup>. There were only five months of complete measurements from the third year between May – September 2010, however during the same period from the previous two years the total accumulation was 12.2 (year 1) and 13.7 (year 2) mol m<sup>-2</sup>, while the same period in the third year accumulated 11.9 mol m<sup>-2</sup>.

## 5.4.4 Carbon balance

As the peatland was found to have inputs and outputs of carbon, the CO<sub>2</sub> and CH<sub>4</sub> components were combined to determine whether the peatland was a source or sink of carbon on a monthly and annual basis as seen in Fig. 5.14 and Table 5.3.

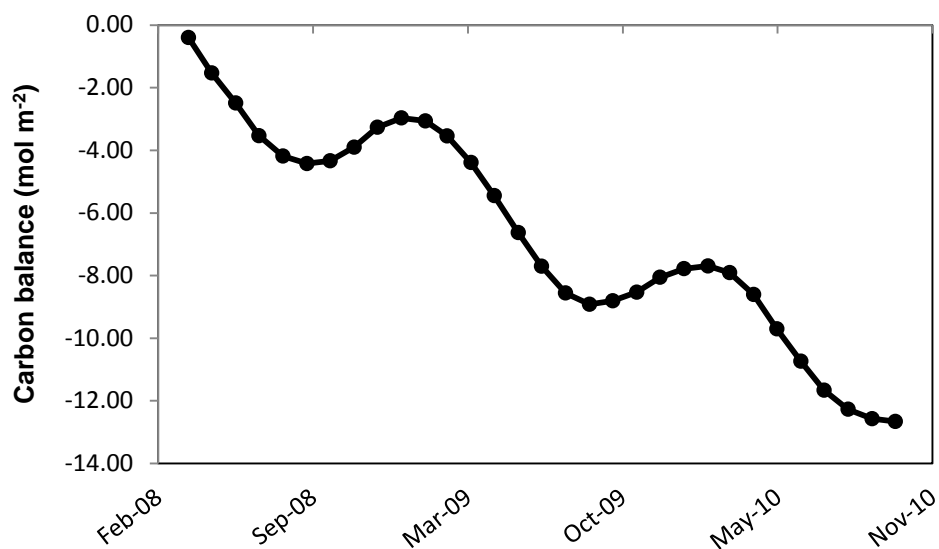


Figure 5.14. Cumulative monthly carbon exchange during the measurement period during 2008 – 2010, based upon eddy covariance CO<sub>2</sub> measurements and estimated CH<sub>4</sub> emissions from chamber measurements.

The balance of the carbon flux was largely driven by the CO<sub>2</sub> exchange as this was by far the larger flux component. The total amount of CO<sub>2</sub> and CH<sub>4</sub> accumulated was 12.66 mol m<sup>-2</sup>. CO<sub>2</sub> alone was responsible for accumulating 12.80 mol m<sup>-2</sup> of carbon over the measurement period, vastly outweighing the amount of carbon released in emissions of CH<sub>4</sub>, which stood at 0.14 mol m<sup>-2</sup>. During the first full year of measurements between May 2009 – April 2009 the net accumulation of carbon was 3.99 mol m<sup>-2</sup> and in the second full year of measurements between May 2009 – April 2010 the accumulation increased slightly to 4.22 mol m<sup>-2</sup>.

Table 5.3. Monthly CO<sub>2</sub>, CH<sub>4</sub> and carbon balance totals for the measurement period.

Month	Total CO <sub>2</sub> uptake (mol m <sup>-2</sup> )	Total CH <sub>4</sub> emission (mmol m <sup>-2</sup> )	Carbon balance (mol m <sup>-2</sup> )
April 2008	-1.20	15.65	-0.40
May 2008	-3.42	39.21	-1.13
June 2008	-2.90	38.32	-0.96
July 2008	-3.16	41.13	-1.05
August 2008	-1.97	35.03	-0.65
September 2008	-0.74	30.81	-0.24
October 2008	0.25	25.93	0.09
November 2008	1.29	24.44	0.43
December 2008	1.90	18.68	0.64
January 2009	0.89	6.59	0.30
February 2009	-0.29	0.09	-0.10
March 2009	-1.44	4.65	-0.48
April 2009	-2.55	9.22	-0.85
May 2009	-3.19	27.69	-1.06
June 2009	-3.56	29.19	-1.18
July 2009	-3.24	28.47	-1.07
August 2009	-2.58	28.46	-0.85
September 2009	-1.10	27.73	-0.36
October 2009	0.32	18.81	0.11
November 2009	0.82	10.09	0.28
December 2009	1.43	5.36	0.48
January 2010	0.82	5.74	0.27
February 2010	0.25	8.00	0.08
March 2010	-0.65	23.46	-0.21
April 2010	-2.11	24.97	-0.70
May 2010	-3.31	27.84	-1.10
June 2010	-3.12	32.99	-1.03
July 2010	-2.80	36.69	-0.93
August 2010	-1.84	30.77	-0.61
September 2010	-0.93	31.96	-0.30
October 2010	-0.27	11.73	-0.09

## 5.4.5 Global warming potential

As CH<sub>4</sub> is known to have a greater warming effect than an equivalent quantity of CO<sub>2</sub> (IPCC 2007), while the quantity of CH<sub>4</sub> emissions were far smaller than the CO<sub>2</sub> uptake, they may still have a significant global warming impact. CH<sub>4</sub> is calculated to have 72 times the warming potential of CO<sub>2</sub> over a 20 year period, decreasing to 25 times and 7.6 times over 100 and 500 years respectively due to the reduced longevity of CH<sub>4</sub> in the atmosphere compared to CO<sub>2</sub>. This increased warming potential has been calculated in Table 5.4.

Table 5.4. The CO<sub>2</sub> and CH<sub>4</sub> total emissions for 2008 – 2010 and the equivalent quantity of CH<sub>4</sub> taking account of the increased warming potential of CH<sub>4</sub>. Note that 2008 and 2010 were not full years of measurements.

Year	CO <sub>2</sub> uptake (mol m <sup>-2</sup> )	CH <sub>4</sub> emissions (mol m <sup>-2</sup> )	Equivalent CH <sub>4</sub> emission accounting for increased GWP		
			20 years	100 years	500 years
2008	-9.95	0.27	19.38	6.73	2.05
2009	-14.49	0.20	14.14	4.91	1.49
2010	-13.96	0.23	16.86	5.85	1.78

As shown in Table 5.4. when the increased global warming potential of CH<sub>4</sub> is taken into account, it becomes a far more considerable factor in the gas exchange of the ecosystem. Over a short period of only 20 years the warming potential of the CH<sub>4</sub> released from the ecosystem exceeded or was roughly equivalent to the warming potential of the CO<sub>2</sub> that was sequestered at the site. However, due to the shorter lifespan of CH<sub>4</sub> in the atmosphere compared to CO<sub>2</sub>, when looked at over a longer time period the warming potential of emitted CH<sub>4</sub> becomes far less significant than the warming potential of CO<sub>2</sub> that was taken up by the site as seen in Fig. 5.15.

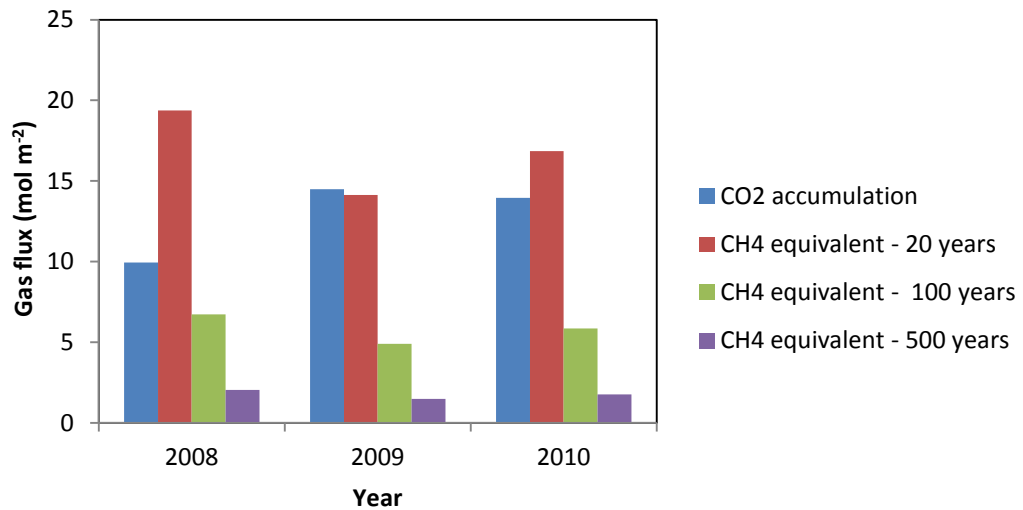


Figure 5.15. The CO<sub>2</sub> accumulation (displayed as a positive value) for individual calendar years, compared to CH<sub>4</sub> emissions, calculated to take account of the increased global warming potential of CH<sub>4</sub> compared to CO<sub>2</sub> over 20, 100 and 500 years.

The Flows Country is considered to be one of the pristine areas of UK peatlands due to the isolated nature of the area resulting in limited pollution and management of the peatlands. As a result it is widely believed that they provide an indication of how a naturally functioning UK peatland would behave. Tables 5.5. and 5.6. show how the measurements of CO<sub>2</sub> and CH<sub>4</sub> fluxes measured at Forsinard in this study compare to similar measurements of annual budgets carried out at peatland sites of varying types within the UK and abroad.

Table 5.5. The annual CO<sub>2</sub> budgets for Forsinard and a selection of similar peatland sites in comparison. The CO<sub>2</sub> budget is expressed as g m<sup>-2</sup> yr<sup>-1</sup>.

Ecosystem	Location	CO <sub>2</sub> budget	Reference
Ombrotrophic bog	Northern Scotland	-41	Beverland <i>et al.</i> 1996
Tundra	Siberia	-38	Corradi <i>et al.</i> 2005
Blanket bog	Northern England	-49 – -58	Worrall <i>et al.</i> 2009
Minerotrophic mire	Northern Finland	-4 – -53	Aurela <i>et al.</i> 2004
Blanket bog	Ireland	-96	Sottocornola 2007
Temperate heath	Denmark	-293	Larsen <i>et al.</i> 2007
Ombrotrophic bog	Southeast Canada	-71	Lafleur <i>et al.</i> 2003
Raised bog	New Zealand	-197	Smith 2003
Blanket bog	Ireland	-66	Sottocornola & Kiely 2005
Ombrotrophic bog	Southern Scotland	-27	Hargreaves <i>et al.</i> 2003
Blanket bog	Northern Scotland	-155.5	This study

Table 5.6. The annual CH<sub>4</sub> budgets for Forsinard and a selection of similar peatland sites in comparison. The CH<sub>4</sub> budget is expressed as g m<sup>-2</sup> yr<sup>-1</sup>.

Ecosystem	Location	Methane budget	Reference
Boreal bog	Ontario, Canada	3.4	Bubier <i>et al.</i> 2003
Blanket bog	Northern England	5.72	Ward <i>et al.</i> 2007
Raised – Blanket bog	Southern Scotland	11.23	Sheppard <i>et al.</i> 2004
Tundra	Siberia	3.15	Wille <i>et al.</i> 2008
Blanket bog	Northern England	5.2 – 6.9	Worrall <i>et al.</i> 2009
Boreal fen	Finland	12.6	Rinne <i>et al.</i> 2007
Blanket bog	Northern Scotland	4.1	This study

## 5.5 Discussion

As anticipated, the peatland was a sink for CO<sub>2</sub> over the course of observations and a source of CH<sub>4</sub>. Overall the uptake of CO<sub>2</sub> by the vegetation significantly exceeded the CH<sub>4</sub> emissions, indicating that the peatland is still a sink for carbon and is still growing. However this did not factor in carbon being lost through water flows off the site as DOC, DIC and POC. This would reduce the size of the sink and if a high export, could potentially turn the peatland into a sink (Billett *et al.* 2004, Worrall *et al.* 2003). As shown in Tables 5.5 and 5.6 the fluxes measured at the site are comparable to other peatland sites within the UK and across the world, appearing to indicate that the ecosystem is in a healthy state, however there were some significant differences between peatland types.

### NEE measurements

The measurements recorded at the site for CO<sub>2</sub> were consistent with those made at other peatland sites in the UK and abroad. Lafleur *et al.* (2001) found a Canadian peatland was an annual sink of 67 g m<sup>-2</sup> y<sup>-1</sup>, while Aurela *et al.* (2002) measured an annual sink of 68 g m<sup>-2</sup> y<sup>-1</sup>. Peatlands will not necessarily have constant sinks of CO<sub>2</sub> as their functioning is dependent on environmental conditions. In Canada it was found that a peatland could shift from a sink of - 260 g m<sup>-2</sup> y<sup>-1</sup> to - 34 g m<sup>-2</sup> y<sup>-1</sup> the next year (Lafleur *et al.* 2003), annual sinks which fall either side of the estimate for Forsinard in this study.

Sottocornola & Kiely (2005) found sinks at a peatland in Ireland of -49 and -61 g m<sup>-2</sup> y<sup>-1</sup> over consecutive years. This type of variation between years was observed at Forsinard, as shown in Figs. 5.9 and 5.13, even though there were no dramatic environmental shifts during the measurement period. This showed the importance of making measurements across multiple years, so that annual budgets are not based on single years consisting of unusual observations.

The CO<sub>2</sub> measurements showed a clear seasonal change from a sink of CO<sub>2</sub> between February/March – September/October and a source of CO<sub>2</sub> between October – January/February. This seasonal cycle is primarily driven by the NPP, which increases activity during summer months due to the increased solar radiation

available. This was consistent with measurements in Canada where a peatland found average summer fluxes of  $-116 \text{ mg m}^{-2} \text{ h}^{-1}$  switching to a winter source of  $45 \text{ mg m}^{-2} \text{ h}^{-1}$  (Lafleur *et al.* 2001). Aurela *et al.* (2002) also found differences between summer and winter fluxes of up to  $-9 \text{ g m}^{-2} \text{ d}^{-1}$  during the summer and  $2.5 \text{ g m}^{-2} \text{ d}^{-1}$  during the winter.

The use of eddy covariance measurement techniques enabled the annual  $\text{CO}_2$  budget to be measured for the site rather than relying on estimates from periodic measurements. It will also enable an examination of how the peatland reacts to different environmental conditions as data is collected over an increasing number of years, therefore enabling predictions of how the site will respond to future climatic conditions. However, this method limits some of the conclusions that can be drawn from the site. Eddy covariance can only measure a general area and the footprint depends on the wind. It is therefore not possible to determine what role specific vegetation types play in the carbon budget, or to examine specific areas of the site, such as gullies, pools or raised outcrops. This means that the flux measurements can only be applied generally to a wider area and cannot be estimated based on the specific ground details outside the footprint of the flux tower.

### **CH<sub>4</sub> measurements**

The annual  $\text{CH}_4$  budget was as expected an overall release of  $\text{CH}_4$  from the land to the atmosphere, although the rates were smaller than those seen for  $\text{CO}_2$ . The annual  $\text{CH}_4$  budget of  $4.1 \pm 0.9 \text{ g m}^{-2} \text{ y}^{-1}$  measured at the site was equivalent to measurements at other blanket bogs, ranging from  $3.4 - 6.9 \text{ g m}^{-2} \text{ y}^{-1}$  (Bubier *et al.* 2003, Ward *et al.* 2007, Worrall *et al.* 2009). The estimated budget however was substantially smaller than that calculated for a raised blanket bog of  $11.2 \text{ g m}^{-2} \text{ y}^{-1}$  (Sheppard *et al.* 2004) and boreal fen of  $12.6 \text{ g m}^{-2} \text{ y}^{-1}$  (Rinne *et al.* 2007).

As one of the drivers of  $\text{CH}_4$  emissions is temperature, the  $\text{CH}_4$  emissions saw a seasonal variation as with  $\text{CO}_2$ , with the largest emissions of  $\text{CH}_4$  during the summer months and smaller emissions during the winter. However, even in winter by these estimates, the peatland acted as a source of  $\text{CH}_4$ , which may be due to the high water table in place at the site. The accuracy of these estimations was limited however, due

to a reduced number of measurements made during winter months as a result of practical difficulties accessing the site. During periods of snow and freezing temperatures, methods of CH<sub>4</sub> transportation are likely to be inhibited and CH<sub>4</sub> emissions reduced. Sachs *et al.* (2008) have suggested that factors affecting the transportation of CH<sub>4</sub> may be more important than temperature in explaining methane fluxes, therefore fluxes may be lower in winter than predicted if transportation is more significantly impacted. An increased frequency of chamber measurements during winter time, or continuous eddy covariance measurements would provide greater understanding of CH<sub>4</sub> emissions over winter.

As expected, the CH<sub>4</sub> emissions were smaller than the CO<sub>2</sub> uptake. It had been hypothesised that CO<sub>2</sub> would be the larger gas exchange, however it was expected that CH<sub>4</sub> would have a greater magnitude if the site was not a fast growing system. The high water table at the site most of the year was thought to be an indicator that high methane emissions could be expected. However, it is possible that the lower than expected fluxes were due to the northerly location of the site within the UK, resulting in lower mean temperatures, which would likely reduce the amount of methane emitted from the site (Davidson & Janssens 2006). However, as seen in Table. 5.6, the fluxes measured were equivalent to those measured at a number of other sites. McNamara *et al.* (2008) found that up to 95 % of CH<sub>4</sub> emissions at peatlands may come from small gully areas inhabited by *Sphagnum* and *Juncus* vegetation. As seen in Fig. 5.1. the site had numerous gullies, which although covering a small area, could be responsible for a large amount of the CH<sub>4</sub> emissions from the site, which would be underestimated by chamber measurements. It is therefore possible that the CH<sub>4</sub> annual budget could be higher or lower if hot spots are taken into account and winter fluxes transpire to be lower than estimated in this study.

### **Carbon balance and global warming effect**

When CO<sub>2</sub> and CH<sub>4</sub> fluxes were combined to look at the carbon balance, the site was found to still be accumulating carbon as the quantity of CO<sub>2</sub> sequestered was significantly larger than the CH<sub>4</sub> emissions. This suggests that the peatland is still a growing peatland ecosystem, however this does not factor in any losses of carbon

through fluvial transport. It is possible that CH<sub>4</sub> fluxes may also be larger than estimated if the distribution of chambers at the site did not account for specific areas of high CH<sub>4</sub> emissions. Annual fluvial carbon losses from UK peatlands have been estimated between 30.4 – 47.0 g m<sup>-2</sup> (Billet *et al.* 2004, Worrall *et al.* 2003). The annual carbon balance measured for CO<sub>2</sub> and CH<sub>4</sub> in this study ranged from 47.9 – 50.7 g m<sup>-2</sup>, and while these estimates exceeded even the highest estimates from Billet *et al.* (2004) and Worrall *et al.* (2003), it does indicate how the carbon sink may be significantly reduced when fluvial fluxes are accounted for.

Although CO<sub>2</sub> accumulation far exceeded the emissions of CH<sub>4</sub> as individual gases and in terms of the carbon balance, when the increased global warming potential of CH<sub>4</sub> was taken into account, it meant CH<sub>4</sub> was a significant factor in terms of greenhouse gas emissions. CH<sub>4</sub> is a more potent greenhouse gas, however has a shorter lifespan in the atmosphere than CO<sub>2</sub>, which means that the impact of it decreases compared to CO<sub>2</sub> over time. When looked at over a 20 year period, the warming effect of the CH<sub>4</sub> emitted from the peatland either matched or exceeded the warming effect of the CO<sub>2</sub> that the ecosystem removed from the atmosphere as seen in Fig. 5.15, however over longer periods of 100 years or more, the effect of the CH<sub>4</sub> became less significant compared to the CO<sub>2</sub>. However, the fact that a small quantity of CH<sub>4</sub> was able to have such a significant effect in terms of global warming, shows that small increases in CH<sub>4</sub> emissions in the future could translate to a more significant change in the role of the ecosystem in terms of global warming, possibly switching from having a cooling effect to a warming effect.

The “ideal” management practice at a site is likely to depend on the priority for the landowner. Restoration of a peatland to a pristine state of high water tables with mosses and dwarf shrub vegetation may have positive benefits for flora and fauna biodiversity, however in terms of carbon storage and greenhouse gas exchange other land uses may be more beneficial. The carbon exchange of this study was consistent with that measured at other sites, as shown in Tables. 5.4 and 5.5., however the use of peatlands for forestry has the capability to dramatically increase the CO<sub>2</sub> uptake of a site, up to 490 – 880 g m<sup>-2</sup> y<sup>-1</sup> (Hargreaves *et al.* 2003, Ojanen *et al.* 2013). Therefore land managers solely interested in mitigating climate change may consider

tree plantations over restoration in order to increase carbon storage. The fact that this study shows that the warming effect of CH<sub>4</sub> emissions may be equivalent to the cooling effect CO<sub>2</sub> uptake over a short time period may be a particular motive for some to consider switching to forestry with the intention to increase CO<sub>2</sub> uptake and reduce CH<sub>4</sub> emissions through drainage.

### **Shortcomings and future work**

As seen in this study, continuous measurements enabled more accurate estimates of the annual budget and fluxes at different times of the year. The measurements of the carbon budget at the site was hindered by the failure of the equipment during the measurement period. Fortunately using the mean daily and monthly values meant it was possible to estimate some of the variables and provide an estimated flux during the period of missing data. However, as continuous measurements were not used for CH<sub>4</sub> this meant that certain environmental conditions that the peatland is expected to be exposed to during the year such as snowfall or drought could not be taken into account or investigated if they did not coincide with a set of planned field measurements.

The remote location of the site limited the number of CH<sub>4</sub> observations it was possible to obtain due to the necessary travelling time. In addition, there were a number of occasions when it was not possible to reach the site due to snow, flooding and hunting, therefore planned flux measurements had to be cancelled. An increased number of CH<sub>4</sub> measurements would have strengthened the regressions used to determine CH<sub>4</sub> flux from environmental variables and therefore improved estimations of CH<sub>4</sub> fluxes at times measurements weren't made. This would also increase the chances of making CH<sub>4</sub> measurements at a time when the peatland is subjected to extreme conditions.

Improvements in peatland budget estimation will come with increased numbers of measurements, whether this refers to longer term measurements or an increased sampling size or frequency, as increased data allows better data modelling and can take into account peatland responses over multiple years. Due to practical considerations, it was only possible to measure 20 chamber locations at the site,

which equated to a total area of only 2.5 m<sup>2</sup>. Improvements in gas flux measurement technology have made it more practical to measure CH<sub>4</sub> using open path eddy covariance methods at remote locations. This offers the ability to make continuous measurements all year round, avoiding the need to model and upscale from chamber measurements covering a small spatial area. Approaches such as this also help to incorporate areas of CH<sub>4</sub> “hot spot” emissions into flux measurements (McNamara *et al.* 2008).

Measurements over a long term period of a number of years will also give insight into the response of the ecosystem to changing environmental conditions, such as increasing temperature and changes in precipitation. Numerous studies have shown changes in CO<sub>2</sub> and CH<sub>4</sub> fluxes over seasonal periods during the same year and between years (Lafleur *et al.* 2001, Aurela *et al.* 2002, Sottocornola & Kiely). This was observed in this study to a minor degree, during years of unremarkable weather. There is a risk that an annual gas exchange budget of a peatland based on only a couple of years measurements may be unrepresentative if those years happened to have abnormal environmental conditions. Observing the reaction of the peatland to varied environmental conditions over a number of years, including extreme rainfall and drought, will increase confidence in the functioning and budget of the ecosystem and in predicting how the ecosystem will behave in possible future climatic scenarios.

## 5.6 Conclusions

As expected, measurements at a pristine peatland in the UK determined that it was still acting as a sink of CO<sub>2</sub> and a source of CH<sub>4</sub>. Over the course of the measurements the peatland acted as an annual sink of CO<sub>2</sub> of 155 g m<sup>-2</sup>, while it was an annual source of CH<sub>4</sub> of 4.1 g m<sup>-2</sup>. Overall the site was determined to be an annual sink for carbon of 49.3 g m<sup>-2</sup>. However, this did not take into account the carbon lost in fluvial transport, which could significantly reduce the carbon uptake.

When the gases were considered in terms of their global warming potential, CH<sub>4</sub> became far more significant. Over a short timescale of less than 20 years, the warming effect of the CH<sub>4</sub> released matched or exceeded that of the CO<sub>2</sub> accumulated. However, over a longer time period of 100 years or more, the warming effect of released CH<sub>4</sub> was significantly less than that of the CO<sub>2</sub> accumulated, due to the shorter lifespan of CH<sub>4</sub> in the atmosphere.

## **CHAPTER 6**

### **SUMMARY, REFERENCES AND APPENDIX**

## 6.1 Summary

This study showed a wide variety of behaviours from peatland ecosystems within the UK. It suggests that carbon exchange varies between sites and even between different areas within sites. The studies undertaken in this thesis are limited due to the short timescale that field measurements must be completed in. Any investigation into these subjects would be improved by longer term studies, which would be able to take into account wider variations in environmental conditions. It may be that some of the relationships and differences seen in this study are the result of specific conditions that existed during the measurement periods such as warmer than average temperatures or higher rainfall than normal. It is also possible that some of the impacts being investigated only become apparent under certain conditions, for example when the ecosystem is stressed due to drought or changing temperatures.

As shown in Chapter 5, this study suggests that sites that have not had significant management are still accumulating carbon over the course of the year within the UK. This is positive news as it suggests that when a UK peatland is considered to be in good condition, it is continuing to store carbon. During the short timescale of this study there appeared to be variations in the amount of carbon exchanged between years as has been found by Lafleur *et al.* (2001), Sottocornola & Kiely (2005) and Billet *et al.* (2004). These measurements found that an undisturbed site with the UK was an annual sink of  $155 \text{ g m}^{-2}$  for  $\text{CO}_2$ , but a small annual source of  $4.1 \text{ g m}^{-2}$  of  $\text{CH}_4$ . However, overall the amount of carbon  $\text{CO}_2$  sequestered outweighed the amount of  $\text{CH}_4$  released and the site was estimated to accumulate  $49.3 \text{ g m}^{-2}$  of carbon annually. However, over a short timescale of less than 20 years, the warming effect of the  $\text{CH}_4$  released was found to match or exceed the  $\text{CO}_2$  sequestered, however the significance of  $\text{CH}_4$  over a longer timescale receded due to the limited lifespan of  $\text{CH}_4$  in the atmosphere and the ecosystem had a net cooling effect. Even so, this indicates just how easily small changes in the size of  $\text{CO}_2$  and  $\text{CH}_4$  fluxes in response to varying environmental conditions, could easily make the ecosystem a net contributor to global warming, even if it remains a sequester of carbon.

While the measurements made in this study showed an overall positive impact of the site on carbon exchange and global warming potential, the measurements are possible skewed by the difference between the continuous measurements of CO<sub>2</sub> and manual measurements of CH<sub>4</sub> used. Improvements in technology provide increased options for continuous measurements of CH<sub>4</sub>, which would remove some of the uncertainties in the estimates created by modelling annual fluxes from a number of periodic measurements covering a small spatial area and time. It is possible that CH<sub>4</sub> fluxes may have been underestimated if they have not taken account of areas of high CH<sub>4</sub> emissions or overestimated by missing periods where CH<sub>4</sub> release is inhibited (McNamara *et al.* 2008). This would also increase the ability to determine the response of CH<sub>4</sub> emissions to the environmental conditions of the site, improving understanding of what drives CH<sub>4</sub> fluxes. With the environment expected to change over the coming decades, this will aid predictions of how the ecosystem will respond, allowing better estimates of feedback to be incorporated into global change models.

An examination of atmospheric pollution and deposition of nitrogen on peatlands in Chapter 3 showed that there was no detectable impact of increasing levels of nitrogen pollution on either vegetation biomass or CO<sub>2</sub> fluxes on a peatland site, Whim Moss. While unexpected, the measurements were made at a site already subjected to significant background atmospheric pollution within the critical load range for ombrotrophic peatlands.

It is therefore possible that any changes in the ecosystem had already occurred even to the control plots. Any further changes that increased nitrogen may have, could therefore be limited by other nutrients or by negative impacts of toxicity on ecosystem functioning caused by excess nitrogen. Conducting a similar experiment at a site, where background nitrogen deposition is much lower or nonexistent may reveal ecosystem changes occurring even at low levels of nitrogen addition. Additionally, expanding the measurements to experimental plots at Whim Moss that had phosphorus and potassium deposition in addition to nitrogen would help reveal whether the limited ecosystem response in vegetation growth and CO<sub>2</sub> fluxes was due to limitations in nutrients other than nitrogen.

Many peatlands in the UK have been subjected to significant pollution in the past due to their proximity to inhabited areas and may therefore not have any reaction to increased levels of pollution in the future as was possibly indicated at Whim Moss. However, currently isolated and pristine peatlands in the UK and abroad may start to experience increased pollution if there is an increase in human activities in these remote areas, for example through increased oil exploitation in Alaska, or if changing weather patterns result in pollution from populated areas being deposited on these peatlands.

While drain blocking previously drained peatlands is now common practice across the UK, it was found to have limited impact upon both the water table and the gas exchange at a field site examined in Chapter 4. The grips only appeared to impact the water table immediately adjacent to them (within 0.5 m) and therefore the blocking of grips that was undertaken only altered this small area immediately adjacent to the grip. Consequently it was found that there was no conclusive effect of grip blocking on gas fluxes or vegetation composition around the grips.

The extremely limited spatial impact of the grips was not expected and it is likely that the impact varies based on the grip dimensions and peatland characteristics such as topography, soil composition and vegetation. As there are a wide variety of grips across many different soil properties an increased sample size may involve grips that have more of an impact on their surrounding area and improve understanding of under what conditions grips are most effective. Coulson *et al.* (1990) suggested that grips in upland peatlands are not as effective as those in lowland areas partly due to higher average rainfall. While this may explain the limited impact seen in Chapter 4, evidence backing this theory may also aid policy makers in deciding which areas should be blocked, to get the largest impact for their money.

The experiment investigating grip blocking in Chapter 4 was limited to examining the first year after blocking took place. However, studies have found that it can take a number of years for grip blocking to have a detectable effect on the surrounding peatland (Bellamy *et al.* 2012, Strack & Zuback 2013). Due to the fact that peatlands tend to react slowly to change it may be a number of years before changes such as vegetation community shifts occur. It is therefore possible a single year after

blocking when these measurements were made was not sufficient time for changes to occur within the peatland and measurements would be needed over a longer timescale to identify longer term impacts of the grip blocking.

In Chapter 3, an effective method of establishing the vegetation biomass without the need to damage the vegetation at the site being investigated was developed at Whim Moss. It was also possible to estimate the LAI and subsequently the NEE flux from a non destructive vegetation survey using simple non technical instruments. This potentially allows NEE to be estimated for numerous locations without the need for expensive equipment. However, when the method was applied to the field site used in Chapter 4, although it correlated well with actual measurements made with CO<sub>2</sub> analysers at the site, it was found to over-estimate the NEE, suggesting that this method was site specific and could not be transferred effectively to another site without calibrating the equations to the site first. It is suggested that this may be due to the method being solely based on vegetation biomass and therefore the calculations do not take account of soil respiration in the flux estimates. However, it is possible that once a series of NEE measurements are made at a new site from new calibration equations can be derived, the method can be used to estimate the flux from other parts of that site.

A common theme from all of the chapters in this thesis was to increase the frequency and length of time over which measurements were made at sites in future work. This allows a more comprehensive examination of impacts that may develop over a number of years, as seen with grip blocking in Chapter 4. As gas fluxes respond directly to environmental conditions, increasing numbers of measurements increase the confidence in how the ecosystem responds to specific conditions. Conducting measurements over extended periods of time increases the range of environmental conditions that the ecosystem will experience. It also enables an understanding of what is normal for the ecosystem and therefore periods of unusual conditions, such as extreme rainfall or temperature can be identified and investigated.

## 6.2 References

- Aerts, R. Chapin, F.S. 2000. The mineral nutrition of wild plants revisited: a re-evaluation of processes and patterns. *Advances in Ecological Research*. 30. 1-67.
- Aldous, A.R. 2002. Nitrogen translocation in *Sphagnum* mosses: effects of atmospheric nitrogen deposition. *New Phytologist*. 156. 241-253.
- Anderson, R.L., Foster, D.R., Motzkin, G. 2003. Integrating lateral expansion into models of peatland development in temperate New England. *Journal of Ecology*. 91. 68-76.
- Aneja V.P., Blunden J., Roelle P.A., Schlesinger W.H., Knighton R., Niyogi D., Gilliam W., Jennings G., Duke C.S. 2008. Workshop on Agricultural Air Quality: State of the science. *Atmospheric Environment*. 42. 3195-3208.
- Armentano, T.V., Menges, E.S. (1986) Patterns of change in the carbon balance of organic-soil wetlands of the temperate zone. *Journal of Ecology*. 74. 755–774.
- Armstrong, A., Holden, J., Kay., P., Foulger, M., Gledhill, S., McDonald, A.T., Walker, A., 2009. Drain-blocking techniques on blanket peat: A framework for best practice. *Journal of Environmental Management*. 90. 3512 – 3519.
- Armstrong, A., Holden, J., Kay, P., Francis, B., Foulger, M., Gledhill, S., McDonald, A.T., Walker, A. 2010. The impact of peatland drain-blocking on dissolved organic carbon loss and discolouration of water; results from a national survey. *Journal of Hydrology*. 38. 112-120.
- Atkinson R., 2000. Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment*. 34. 2063-2101.

Aubinet, M., Vesala, T., Papale, D. 2012. Eddy covariance. A practical guide to measurement and data analysis. Springer Atmospheric Sciences.

Aurela, M., Laurila, T., Tuovinen, J.P. (2002) Annual CO<sub>2</sub> balance of a subarctic fen in northern Europe: Importance of the wintertime efflux. *Journal of Geophysical Research-Atmospheres*, 107, 4607.

Aurela, M., Laurila, T. & Tuovinen, J. P. (2004) The timing of snow melt controls the annual CO<sub>2</sub> balance in a subarctic fen. *Geophysical Research Letters*, 31.

Baldocchi, D.D. 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. *Global Change Biology*. 9. 479-492.

Bartlett, K.B., Harriss, R.C., 1993. Review and assessment of methane emissions from wetlands. *Chemosphere*. 26. 261-320.

Bellamy, P.E., Leigh, A., Maclean, I.S., Grant, M.C. 2012. Response of blanket bog vegetation to drain-blocking. *Applied Vegetation Science*. 15. 129-135.

Belyea, L.R., Malmer, N. 2004. Carbon sequestration in peatland: patterns and mechanisms of response to climate change. *Global Change Biology*. 10. 1043-1052.

Berendse, F., Breemen, N. V., Rydin, H., Buttler, A., Heijmans, M., Hoosbeek, M.R., Lee, J.A., Mitchell, E., Saarinen, T., Vasander, H., Wallén, B. 2001. Raised atmospheric CO<sub>2</sub> levels and increased N deposition cause shifts in plant species composition and production in *Sphagnum* bogs. *Global Change Biology*. 7. 591-598.

Berg, A., Danielsson, Å., Svensson, B.H. 2013. Transfer of fixed-N from N<sub>2</sub>-fixing cyanobacteria associated with the moss *Sphagnum riparium* results in enhanced growth of the moss. *Plant soil*. 362. 271-278.

Beverland, I.J., Moncrieff, J.B., O'Neill, D.H., Hargreaves, K.J., Milne, R., 1996. Measurement of methane and carbon dioxide fluxes from peatland ecosystems by the conditional – sampling technique. *Quarterly Journal of the Royal Meteorological Society*. 122. 819-838.

Billett, M., Palmer, S. M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K. J., Flechard, C., Fowler, D. (2004) Linking land-atmosphere-stream carbon fluxes in a lowland peatland system. *Global Biogeochemical Cycles*, 18.

Blodau, C. 2002. Carbon cycling in peatlands – A review of processes and controls. *Environmental reviews*. 10. 111-134.

Blodau, C., Basiliko, N., Moore, T.R. 2004. Carbon turnover in peatland mesocosms exposed to different water table levels. *Biogeochemistry*. 67. 331-351.

Bragazza, L., Buttler, A., Habermacher, J., Brancaloni, L., Gerdol, R., Fritze, H., Hanajik, P., Laiho, R., Johnson, D., 2012. High nitrogen deposition alters the decomposition of bog plant litter and reduces carbon accumulation. *Global Change Biology*. 18. 1163-1172.

Brooks, S.J. 1997. Peatland dragonflies (Odonata) in Britain: a review of their distribution, status and ecology. In: Parkyn, L., Stoneman, R. E., Ingram, H. A. P. (Eds.) *Conserving peatlands*. Guildford and King's Lynn, CAB International.

Bubier, J.L., Moore, T.R., Roulet, N.T., 1993. Methane emissions from wetlands in the midboreal region of northern Ontario, Canada. *Ecology*. 74. 2240 – 2254.

Bubier, J.L., Moore, T.R., Bledzki, A. 2007. Effects of nutrient addition on vegetation and carbon cycling in an ombrotrophic bog. *Global change biology*. 13. 1-9.

Buringh, P. (1984) Organic carbon in soils of the world. In:Woodwell GM (ed) The role of terrestrial vegetation in the global carbon cycle, SCOPE 23.Wiley, New York. 91–109.

Burt, T.P., Pinay, G., Matheson, F.E., Haycock, N.E., Butturini, A., Clement, J.C., Danielescu, S., Dowrick, D.J., Hefting, M.M., Hillbricht-Ilkowska, A. & Maitre, V. 2002. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. *Journal of Hydrology*. 265. 129-148.

Campbell, I.D., Campbell, C., Yu Z., Vitt D.H., Apps M.J. 2000. Millennial-Scale Rhythms in Peatlands in the Western Interior of Canada and in the Global Carbon Cycle. *Quaternary Research*. 54. 155-158.

Cao, M., Woodward, F.I. 1998. Net primary and ecosystem production and carbon stocks of terrestrial ecosystems and their responses to climate change. *Global change biology*. 4. 185-198.

Carroll, J.A., Caporn, S.J.M., Cawley, L., Read, D.J., Lee, J.A. 1999. The effect of increased deposition of atmospheric nitrogen on *Calluna vulgaris* in upland Britain. *New Phytologist*. 141. 423-431.

Chapman, S.B., 1979. Some interrelationships between soil and root respiration in lowland *Calluna* heathland in southern England. *Journal of Ecology*. 67. 1-20.

Charman, D., 2002. Peatlands and Environmental Change. John Wiley & Sons Ltd.

- Cleary, J., Roulet, N. T., Moore, T.R. 2005. Greenhouse Gas Emissions from Canadian Peat Extraction, 1990–2000: A Life-cycle Analysis. *Ambio*. 34. 456-461.
- Clymo, R.S., 1984 The limits to peat bog growth. *Philosophical Transactions of the Royal Society of London*. B 303. 605-654.
- Clymo, R.S., Bryant, C.L. 2008. Diffusion and mass flow of dissolved carbon dioxide, methane, and dissolved organic carbon in a 7-m deep raised peat bog. *Geochimica et Cosmochimica Acta*. 72. 2048-2066.
- Clymo, R.S., Hayward, P.M. 1982. The ecology of *Sphagnum*. In: Smith, A.J.E. (Ed.) *Bryophyte ecology*. London: Chapman and Hall ltd, 511.
- Clymo, R.S., Turunen, J., Tolonen, K. 1998. Carbon accumulation in peatland. *Oikos*. 81. 368–388.
- Corradi, C., Kolle, O., Walter, K., Zimov., S.A., Schulze, E.D., 2005. Carbon dioxide and methane exchange of a north-east Siberian tussock tundra. *Global Change Biology*. 11. 1910 – 1925.
- Coulson, J.C., Butterfield, J.E.L., Henderson, E. 1990. The effect of open drainage ditches on the plant and invertebrate communities of moorland and on the decomposition of peat. *The Journal of Applied Ecology*. 27 (2). 549-561.
- CTCD. 2007. CTCD Annual Report 2006/7. Centre for Terrestrial Carbon Dynamics (CTCD).
- Davidson, E. A., Janssens, I. A. 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*. 440. 7081. 165-173.

Diolaiuti, G., Smiraglia, C., 2010. Changing glaciers in a changing climate: how vanishing geomorphosites have been driving deep changes in mountain landscapes and environments. *Geomorphologie-relief processus environnement. 2.* 131-152.

Dittman J.A., Driscoll C.T., Groffman P.M., Fahey T.J. 2007. Dynamics of nitrogen and dissolved organic carbon at the Hubbard Brook Experimental Forest. *Ecology.* 88. 1153-1166.

Edwards, G.C., Neumann, H.H., den Hartog, G., Thurtell, G.W., Kidd, G. 1994. Eddy correlation measurements of methane fluxes using a tunable diode laser at the Kinosheo Lake tower site during the Northern Wetlands Study (NOWES). *Journal of Geophysical Research.* 99. 1511-1517.

English Nature 2003: England's best wildlife and geological sites. The condition of Sites of Special Scientific Interest in England in 2003. Peterborough: English Nature, 118 pp.

Evans, R. 1997. Soil erosion in the UK initiated by grazing animals: a need for a national survey. *Applied Geography.* 17. 127-141.

Evans, C. D., Freeman, C., Monteith, D. T., Reynolds, B., Fenner, N. 2002. Terrestrial export of organic carbon- reply to Tranvik, L. J. and Jansson, M. *Nature.* 415. 862.

Evans, C. D., Monteith, D. T., Cooper, D. M. 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution.* 137. 55-71.

Fang, C., Moncrieff, J.B. 1996. An improved dynamic chamber technique for measuring CO<sub>2</sub> efflux from the surface of soil. *Functional Ecology.* 10. 297-305.

Freeman, C., Ostle, N., Kang, H. 2001a. An enzymic 'latch' on a global carbon store. *Nature*. 409. 149.

Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., Fenner, N. 2001b. Export of organic carbon from peat soils. *Nature*. 412. 785.

Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M. A., Sleep, D., Hughes, S., Hudson, J. 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature*. 430. 195-198.

Fritz, C., van Dijk, G., Smolders, A.J.P., Pancotto, V.A., Elzenga, T.J.T.M., Roelofs, J.G.M., Grootjans, A.P. 2012. Nutrient additions in pristine Patagonian *Sphagnum* bog vegetation: can phosphorus addition alleviate (the effects of) increased nitrogen loads. *Plant Biology*. 14. 491-499.

Galloway J.N., Schlesinger W.H., Levy H., Michaels A., Schnoor J.L., 1995. Nitrogen fixation: Anthropogenic enhancement-environmental response. *Global Biogeochemical Cycles* 9, 235-252.

Galloway, J. N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., Vörösmarty, C.J. 2004. Nitrogen cycles: past, present, and future. *Biogeochemistry*. 70. 153-226.

Garnett, M., Ineson, P., Stevenson, A.C. 2000. Effects of burning and grazing on carbon sequestration in a Pennine blanket bog. *The Holocene*. 10. 729-736.

GEC & WI. (2008). Assessment on Peatlands, Biodiversity and Climate change. Main Report. Published by Global Environment Centre, Kuala Lumpur & Wetlands International, Wageningen.

- Gorham, E., Lehman, C., Dyke, A., Clymo, D., Janssens, J. 2012. Long-term carbon sequestration in North American peatlands. *Quaternary Science Reviews*. 58. 77-82.
- Goulden, M.L., Munger, J.W., Fan, S., Daube, B.C., Wofsy, S.C. 1996. Measurements of carbon sequestration by long-term eddy covariance: methods and a critical evaluation of accuracy. *Global Change Biology*. 2. 169-182.
- Graglia, E., Jonasson, S., Michelsen, A., Schmidt, I.K., Havström, M., Gustavsson, L. 2001. Effects of environmental perturbations on abundance of subarctic plants after three, seven and ten years of treatments. *Ecography*. 24. 5-12.
- Greenup, A.L., Bradford, M.A., McNamara, N.P., Ineson, P. & Lee, P. 2000 The role of *Eriophorum vaginatum* in CH<sub>4</sub> flux from an ombrotrophic peatland. *Plant and Soil*. 227. 265-272.
- Griffiths, H., Jarvis, P.G., 2005. *The Carbon Balance of Forest Biomes*. 269-291. Taylor & Francis Group.
- Gruber, N., Galloway, J.N., 2008. An earth system perspective of the global nitrogen cycle. *Nature*. 451. 93-296.
- Gu, F., Zhang, Y., Tao, B., Wang, Q., Yu, G., Zhang, L., Li, K., 2010. Modeling the effects of nitrogen deposition on carbon budget in two temperate forests. *Ecological Complexity*. 7. 139-148.
- Hargreaves, K. J., Fowler, D. 1998 Quantifying the effects of water table and soil temperature on the emission of methane from peat wetland at the field scale. *Atmospheric Environment*. 32. 3275-3282.
- Hargreaves, K.J., Fowler, D., Pitcairn, C.E.R., Aurela, M. 2001. Annual methane emission from Finnish mires estimated from eddy covariance campaign measurements. *Theoretical and Applied Climatology*. 70. 203-213.

Hargreaves, K.J., Milne, R., Cannell, M.G.R., 2003. Carbon balance of afforested peatlands in Scotland. *Forestry*. 76. 299 – 317.

Hayati, A. A., Proctor, M.C.F., 1991. Limiting nutrients in acid-mire vegetation: peat and plant analyses and experiments on plant responses to added nutrients. *Journal of Ecology* 79(1): 75-95.

Heeb N.V., Saxer C.J., Forss A.-M., Bruhlmann S. 2008. Trends of NO-, NO<sub>2</sub>-, and NH<sub>3</sub>-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars. *Atmospheric Environment*. 42. 2543-2554.

Heijmans, M.M.P.D., Berendse, F., Arp, W.J., Masselink, A.K., Klees, H., De Visser, W., Van Breemen, N. 2001. Effects of elevated carbon dioxide and increased nitrogen deposition on bog vegetation in the Netherlands. *Journal of Ecology*. 89. 268-279.

Heinemeyer, A., Di Bene, C., Lloyd, A.R., Tortorella, D., Baxter, R., Huntley, B., Gelsomino, A., Ineson, P. 2011. Soil respiration: implications of the plant-soil continuum and respiration chamber collar-insertion depth on measurement and modelling of soil CO<sub>2</sub> efflux rates in three ecosystems. *European Journal of Soil Science*. 62. 82-94.

Heinemeyer, A., Gruber, V., Bahn, M. 2012. The ‘Gas-Snake’: Design and validation of a versatile membrane-based gas flux measurement system in a grassland soil respiration study. *Agricultural and Forest Meteorology*. 154-155. 166-173.

Holden, J. 2005. Peatland hydrology and carbon release: why small-scale process matters. *Philosophical Transactions of the Royal Society*. 363. 2891-2913.

Holden, J., Burt, T.P., 2002. Laboratory experiments on drought and runoff in blanket peat. *European Journal of Soil Science*. 53. 675-689.

Holden, J., Chapman, P.J., Lane, S.N., Brookes, C.J., 2006. Impacts of artificial drainage of peatlands on runoff production and water quality. In: *Peatlands: Evolution and records of environmental and climate changes*. Elsevier, Amsterdam. 501 – 528.

Holden, J., Chapman, P.J., Labadz, J.C. 2004. Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration. *Progress in Physical Geography*. 28(1). 95-123.

Holden, J., Chapman, P., Evans, M., Hubacek, K., Kay, P., Warburton, J. 2006b. Vulnerability of organic soils in England and Wales. Final technical report to DEFRA, Project SP0532.

Holden, J., Shotbolt, L., Bonn, A., Burt, T.P., Chapman, P.J., Dougill, A.J., Fraser, E.D.G., Hubacek, K., Irvine, B., Kirkby, M.J., Reed, M.S., Prell, C., Stagl, S., Stringer, L.C., Turner, A., Worrall, F., 2007a. Environmental change in moorland landscapes. *Earth-Science Reviews*. 82. 75-100.

Holden, J., Gascoign, M., Bosanko, N.R., 2007b. Erosion and natural revegetation associated with surface land drains in upland peatlands. *Earth surface processes and landforms*. 32. 1547 – 1557.

Hoosbeek, M.R., Van Breemen, N., Vasander, H., Buttler, A., Berendse, F. 2002. Potassium limits potential growth of bog vegetation under elevated atmospheric CO<sub>2</sub> and N deposition. *Global Change Biology* 8: 1130-1138.

- Huang, C.C., O'Connell, M. 2000. Recent land-use and soil erosion history within a small catchment in Connemara, western Ireland: evidence from lake sediments and documentary sources. *Catena*. 41. 293- 335.
- IPCC, 2007. *Climate Change 2007. The physical science basis. Contribution of working group 1 to the fourth assessment report of the intergovernmental panel on climate change.* Cambridge University Press.
- Janssens, I.A., Kowalski, A.S., Ceulemans, R. 2001. Forest floor CO<sub>2</sub> fluxes estimated by eddy covariance and chamber-based model. *Agricultural and Forest Meteorology*. 106. 61-69.
- Jensen, L.S., Mueller, T., Tate, K.R., Ross, D.J., Magid, J. & Nielsen, N.E. 1996. Soil surface CO<sub>2</sub> flux as an index of soil respiration in situ: a comparison of two chamber methods. *Soil Biology and Biochemistry*. 28. 1297-1306.
- Joiner, D. W., Lafleur, P. M., McCaughey, J. H. & Bartlett, P. A. (1999) Interannual variability in carbon dioxide exchanges at a boreal wetland in the BOREAS northern study area. *Journal of Geophysical Research-Atmospheres*. 104. 27663-27672.
- Jones D.L., Willett V.B. 2006. Experimental evaluation of methods to quantify dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in soil. *Soil Biology and Biochemistry*. 38. 991-999.
- Joosten, H., Clarke, D., 2002. *Wise use of mires and peatlands – Background and principles including a framework for decision-making.* International Mire Conservation Group / International Peat Society.
- Juutinen, S., Bubier, J.L., Moore, T.R., 2010. Responses of vegetation and ecosystem CO<sub>2</sub> exchange to 9 years of nutrient addition at Mer Bleue Bog. *Ecosystems*. 13. 874-887.

Keddy, P.A., Fraser, L.H., Solomeshch, A.I., Junk, W.J., Campbell, J.R., Arroyo, M.T.K., Alho, C.J.R. 2009. Wet and wonderful: The world's largest wetlands are conservation priorities. *Bioscience*. 59(1). 39-51.

Knorr, W., Prentice, I.C., House, J.I., Holland, E.A. 2005. Long-term sensitivity of soil carbon turnover to warming. *Nature*. 433. 298-300.

Koch, O., Tschirko, D., Kandeler, E. 2007. Seasonal and Diurnal Net Methane Emissions from Organic Soils of the Eastern Alps, Austria: Effects of Soil Temperature, Water Balance, and Plant Biomass. *Arctic, Antarctic and Alpine Research*. 39. 3. 438-448.

Komulainen, V-M., Stiina, Tuittila, E-S., Vasander, H., Laine, J. 1999. Restoration of drained peatlands in southern Finland: initial effects on vegetation change and CO<sub>2</sub> balance. *Journal of Applied Ecology*. 36. 634-648.

Koven, C., Friedlingstein, P., Ciais, P., Khvorostyanov, D., Krinner, G., Tarnocai, C. 2009. On the formation of high-latitude soil carbon stocks: Effects of cryoturbation and insulation by organic matter in a land surface model. *Geophysical research letters*. 36. L21501.

Kroon, P.S., Hensen, A., van den Bulk, W.C.M., Jongejan, P.A.C., Vermeulen, A.T., 2008. The importance of reducing the systematic error due to non-linearity in N<sub>2</sub>O flux measurements by static chambers. *Nutrient Cycling in Agroecosystems*. 82. 175-186.

Kutsch, W.L., Bahn, M., Heinemeyer, A. 2010. *Soil Carbon Dynamics: An Integrated Methodology*. Cambridge University Press.

Kutzbach, L., Schneider, J., Sachs, T., Giebels, M., Nykänen, H., Shurpali, N.J., Martikainen, P.J., Alm, J., Wilmking, M. 2007. CO<sub>2</sub> flux determination by closed-

chamber methods can be seriously biased by inappropriate application of linear regression. *Biogeosciences*. 4. 1005-1025.

Lafleur, P.M., Roulet, N.T., Bubier, J.L., Frohling, S., Moore, T.R., 2003. Interannual variability in the peatland-atmosphere carbon dioxide exchange at an ombrotrophic bog. *Global Biogeochemical Cycles*. 17. 1036.

Lafleur, P. M., Roulet, N. T. & Admiral, S. W. (2001) Annual cycle of CO<sub>2</sub> exchange at a bog peatland. *Journal of Geophysical Research- Atmospheres*, 106 3071-3081.

Laine, J., Vasander, H., Laiho, T. 1995. Long-term effects of water level drawdown on the vegetation of drained pine mires in southern Finland. *Journal of Applied Ecology*. 32. 785-802.

Lamarque, J. F., Kiehl, J.T., Brasseur, G.P., Butler, T., Cameron-Smith, P., Collins, W.D., Collins, W.J., Granier, C., Hauglustaine, D., Hess, P.G., Holland, E.A., Horowitz, L., Lawrence, M.G., McKenna, D., Merilees, P., Prather, M.J., Rasch, P.J., Rotman, D., Shindell, D., Thornton, P. 2005. Assessing future nitrogen deposition and carbon cycle feedback using a multimodel approach: Analysis of nitrogen deposition. *Journal of Geophysical Research*. 110.

Lamers, L.P.M., Bobbink, R., Roelofs, J.G.M. 2000. Natural nitrogen filter fails in polluted raised bogs. *Global change biology*. 6. 583-586.

Larsen, K.S., Ibrom, A., Beier, C., Jonasson, S., Michelsen, A., 2007. Ecosystem respiration depends strongly on photosynthesis in a temperate heath. *Biogeochemistry*. 85. 201 – 213.

Levy, P.E., Gray, A., Leeson, S.R., Gaiawyn, J., Kelly, M.P.C., Cooper, M.D.A., Dinsmore, K.J., Jones, S.K., Sheppard, L.J., 2011. Quantification of uncertainty in

trace gas fluxes measured by the static chamber method. *European Journal of Science*. 62. 811-821.

Levy, P.E., Burden, A., Cooper, M.D.A., Dinsmore, K.J., Drewer, J., Evans, C., Fowler, D., Gaiawyn, J., Gray, A., Jones, S.K., Jones, T., Mcnamara, N.P., Mills, R., Ostle, N., Sheppard, L.J., Skiba, U., Sowerby, A., Ward, S.E., Zielinski, P. 2012. Methane emissions from soils: synthesis and analysis of a large UK data set. *Global Change Biology*. 18. 1657-1669.

Le Mer, J., Roger, P., 2001. Production, oxidation, emission and consumption of methane by soils: A review. *European Journal of Soil Biology*. 37. 25-50.

Lilly, A. 1998. The use of inverse modelling and dipwell data in the calibration and evaluation of a soil water simulation model. *Geoderma*. 90. 203-227.

Limpens, J., Berendse, F. 2003. How litter quality affects mass loss and N loss from decomposing Sphagnum. *Oikos*. 103. 537-547.

Limpens, J., Berendse, F., Blodau, C., Canadell, J.G., Freeman, C., Holden, J., Roulet, N., Rydin, H., Schaepman-Strub, G. 2008. Peatlands and the carbon cycle: from local processes to global implications – a synthesis. *Biogeosciences*. 5 1475-1491.

Limpens, J., Granath, G., Gunnarsson, U., Aerts, R., Bayley, S., Bragazza, L., Bubier, J., Buttler, A., van den Berg, L.J.L., Francez, A-J., Gerdol, R., Grosvernier, P., Heijmans, M.M.P.D., Hoosbeek, M.R., Hotes, S., Ilomets, M., Leith, I., Mitchell, E.A.D., Moore, T., Nilsson, M.B., Nordbakken, J-F., Rochefort, L., Rydin, H., Sheppard, L.J., Thormann, M., Wiedermann, M.M., Williams, B.L., Xu B., 2011. Climatic modifiers of the response to nitrogen deposition in peat forming Sphagnum mosses: a meta analysis. *New Phytologist*. 191. 496-507.

Livingston, G.P., Hutchinson, G.L., 1995. Enclosure based measurement of trace gas exchange: applications and sources of error. In: *Methods in Ecology. Biogenic trace gases: Measuring emissions from soil and water.* [Matson, P.A., Harriss, R.C., (eds.)] Blackwell Science, Blackwell Publishing, Oxford.

MacDonald, G.M., Beilman, D.W., Kremenetski, K.V., Sheng, Y., Smith, L.C., Velichko, A.A. 2006. Rapid early development of circumarctic peatlands and atmospheric CH<sub>4</sub> and CO<sub>2</sub> variations. *Science*. 314. 285- 288.

McNamara, N. P., Plant, T., Oakley, S., Ward, S., Wood, C., Ostle, N. 2008. Gully hotspot contribution to landscape methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) fluxes in a northern peatland. *Science of The Total Environment*, 404, 354-360.

Malmer, N., Albinsson, C., Svensson, B.M., Wallén, B. 2003. Interferences between Sphagnum and vascular plants: effects on plant community structure and peat formation. *Oikos*. 100 469-482.

Malmer, N., Wallén, B., 2005. Nitrogen and phosphorus in mire plants: variation during 50 years in relation to supply rate and vegetation type. *Oikos*. 109. 539-554

Marsden, K., Ebmeier, S. 2012. Peatlands and Climate Change. SPICe Briefing, The Scottish Parliament.

McHugh, M., Harrod, T., Morgan, R. 2002. The extent of soil erosion in Upland England and Wales. *Earth Surface Processes and Landforms*. 27. 99-107.

Meehl, G.A., Hu, A.X., Tebaldi, C., Arblaster, J.M., Washington, W.M., Teng, H.Y., Sanderson, B.M., Ault, T., Strand, W.G., White, J.B., 2012. Relative outcomes of climate change mitigation related to global temperature versus sea-level rise. *Nature climate change*. 2. 576-580.

Milne, R., Brown, T.A., 1997. Carbon in the vegetation and soils of Great Britain. *Journal of Environmental Management*. 49. 413-433.

Montanarella, L., Jones, R.J.A., Hiederer, R., 2006. The distribution of peatland in Europe. *Mires and Peat*. 1. 1-10.

Moncrieff, J.B., Malhi, Y., Leuning, R. 1996. The propagation of errors in long-term measurements of carbon and water. *Global Change Biology*. 2. 231-240.

Moore, T. R., Bubier, J. L., Frohking, S. E., Lafleur, P. M. & Roulet, N. T. (2002) Plant biomass and production and CO<sub>2</sub> exchange in an ombrotrophic bog. *Journal of Ecology*, 90, 25-36.

Minkinen, K., Laine, J., 2006. Vegetation heterogeneity and ditches create spatial variability in methane fluxes from peatlands drained for forestry. *Plant and Soil*. 285. 289-304.

Mueller, S.D., Richard, P.J.H., Larouche, A.C. 2003. Holocene development of a peatland (southern Québec): a spatio-temporal reconstruction based on pachymetry, sedimentology, microfossils and macrofossils. *The Holocene*. 13. 649-664.

Nakayama, F.S. 1990. Soil respiration. *Remote Sensing. Reviews*. 5. 311-321.

NCC 1987. Birds, bogs and forestry. The peatlands of Caithness and Sutherland. Interpretive Services Branch.

Nitro Europe 2011. The nitrogen cycle and its influence on the European greenhouse gas balance. Source: [www.nitroeuropa.eu](http://www.nitroeuropa.eu).

Nohrstedt, H.-Ö, Arnebrant, K., Bååth, E., Söderström, B. 1989. Changes in carbon content, respiration rate, ATP content, and microbial biomass in nitrogen-fertilized pine forest soils in Sweden. *Canadian Journal of Forest Research*. 19(3) 323-328.

- Nordbakken, J.F., Ohlson, M., Högberg, P. 2003. Boreal bog plants: nitrogen sources and uptake of recently deposited nitrogen. *Environmental Pollution*. 123. 191-200.
- Nordin, A., Gunnarsson, U. 2000. Amino acid accumulation and growth of *Sphagnum* under different levels of N deposition. *Ecoscience*. 7(4). 474-480.
- Norman, J.M., Kucharik, C.J., Gower, S.T., Baldocchi, D.D., Crill, P.M., Rayment, M., Savage, K., Striegl, R.G. 1997. A comparison of six methods for measuring soil-surface carbon dioxide fluxes. *Journal of Geophysical Research*. 102. 28771-28777.
- North Pennines AONB. North Pennines Area of Outstanding Beauty website [www.northpennines.org.uk](http://www.northpennines.org.uk).
- Ohlson, M., Okland, R. H. 1998. Spatial variation in rates of carbon and nitrogen accumulation in a boreal bog. *Ecology*. 79. 2745-2758.
- Ojanen, P., Minkkinen, K., Penttilä, T. 2013. The current greenhouse gas impact of forestry-drained boreal peatlands. *Forest Ecology and Management*. 289. 201-208.
- Parish, F., Sirin, A., Charman, D., Joosten, H., Minayeva, T., Silvius, M. and Stringer, L. (Eds.) 2008. *Assessment on Peatlands, Biodiversity and Climate Change: Main Report*. Global Environment Centre, Kuala Lumpur and Wetlands International, Wageningen.
- Pastor, J., Solin, J., Bridgham, S. D., Updegraff, K., Harth, C., Weishampel, P., Dewey, B. 2003. Global warming and the export of dissolved organic carbon from boreal peatlands. *OIKOS*. 100, 380-386.
- Pearce-Higgins, J., Dennis, P., Whittingham, M., Yalden, D. 2009. Impacts of climate on prey abundance account for fluctuations in a population of a northern wader at the southern edge of its range. *Global Change Biology*. 16 (1). 12–23.

Petit C., Bandosz T.J. 2008. Removal of ammonia from air on molybdenum and tungsten oxide modified activated carbons. *Environmental Science & Technology*. 42. 3033-3039.

Pfeiffer, S.M., Bahr, J.M. & Beilfuss, R.D. 2006. Identification of groundwater flowpaths and denitrification zones in a dynamic floodplain aquifer. *Journal of Hydrology*. 325. 262-272.

Piao, S., Tan, K., Nan, H., Ciais, P., Fang, J., Wang, T., Vuichard, N., Zhu, B. 2012. Impacts of climate and CO<sub>2</sub> changes on the vegetation growth and carbon balance of Qinghai–Tibetan grasslands over the past five decades. *Global and planetary change*. 98-99. 73-80.

Pidwirny, M. (2006). "Acid Precipitation". *Fundamentals of Physical Geography*, 2nd Edition. <http://www.physicalgeography.net/fundamentals/8h.html>

Poulin, M., Andersen, R., Rochefort, L. 2013. A new approach for tracking vegetation change after restoration: A case study with peatlands. *Restoration Ecology*. 21 (3). 363-371.

Powelson, D. 2005. Will soil amplify climate change? *Nature*. 433. 204 – 205.

Prins, A.H., Berdowski, J.J.M., Latuhihin, M.J., 1991. Effect of NH<sub>4</sub><sup>+</sup> fertilization on the maintenance of a *Calluna vulgaris* vegetation. *Acta Botanica Neerlandica*. 40. 269-279.

Pumpanen, J., Kolari, P., Ilvesniemi, H., Minkkinen, K., Vesala, T., Niinisto, S., Lohila, A., Larmola, T., Morero, M., Pihlatie, M., Janssens, I., Curiel Yuste, J., Grünzweig, J.M., Reth, S., Subke, J-A., Savage, K., Kutsch, W., Østreg, G., Ziegler, W., Anthoni, P., Lindroth, A., Hari, P. 2004. Comparison of different

chamber techniques for measuring soil CO<sub>2</sub> efflux. *Agricultural and Forest Meteorology*. 123. 159-176.

Qian, H. Joseph, R., Zeng, N. 2010. Enhanced terrestrial carbon uptake in the Northern High Latitudes in the 21<sup>st</sup> Century from the Coupled Carbon Cycle Climate Model Intercomparison Project model projections. *Global Change Biology*. 16. 641-656.

Ramchunder, S.J., Brown, L.E., Holden, J. 2009. Environmental effects of drainage, drain-blocking and prescribed vegetation burning in UK upland peatlands. *Progress in Physical Geography*. 33(1). 49-79.

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., Bernhofer, C., Buchmann, N., Gilmanov, T., Granier, A., Grünwald, T., Havránková, K., Ilvesniemi, H., Janous, D., Knohl, A., Laurila, T., Lohila, A., Loustau, D., Matteucci, G., Meyers, T., Miglietta, F., Ourcival, J., Pumpanen, J., Rambal, S., Rotenberg, E., Sanz, M., Tenhunen, J., Seufert, G., Vaccari, F., Vesala, T., Yakir, D., Valentini, R. 2005. On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*. 11. 1424-1439.

Reth, S., Göckede, M., Falge, E. 2005. CO<sub>2</sub> efflux from agricultural soils in Eastern Germany - comparison of a closed chamber system with eddy covariance measurements. *Theoretical and Applied Climatology*. 80. 105-120.

Rinne, J., Riutta, T., Pihlatie, M., Aurela, M., Haapanala, S., Tuovinen, J.-P., Tuittila, E.-S., Vesala, T. 2007. Annual cycle of methane emission from a boreal fen measured by the eddy covariance technique. *Tellus B*, 59, 449-457.

Ruppel, M., Väiliranta, M., Virtanen, T., Korhola, A. 2013. Postglacial spatiotemporal peatland initiation and lateral expansion dynamics in North America and northern Europe. *Holocene*. 23(11) 1596-1606.

Rydin, H. & Clymo, R.S. 1989. Transport of carbon and phosphorus compounds about *Sphagnum*. Proceedings of the Royal Society of London. Series B, Biological Sciences 237: 63-84.

Rydin, H., Jeglum, J., 2006. The biology of peatlands. Oxford University Press.

Saarnio, S., Järviö, S., Saarinen, T., Vasander, H., Silvola, J. 2003. Minor changes in vegetation and carbon gas balance in a boreal mire under a raised CO<sub>2</sub> or NH<sub>4</sub>NO<sub>3</sub> supply. Ecosystems. 6. 46-60.

Sachs, T., Wille, C., Boike, J., Kutzbach, L. 2008. Environmental controls on ecosystem-scale CH<sub>4</sub> emission from polygonal tundra in the Lena River Delta, Siberia. Journal of Geophysical Research, 113.

Savage, K.E., Davidson, E.A. 2003. A comparison of manual and automated systems for soil CO<sub>2</sub> flux measurements: trade-offs between spatial and temporal resolution. Journal of Experimental Botany. 54. 891-899.

Scharenbroch B.C., Lloyd J.E. 2004. A literature review of nitrogen availability indices for use in urban landscapes. Journal of Arboriculture. 30. 214-230.

Schipper, L.A., McLeod, M. 2002. Subsidence rates and carbon loss in peat soils following conversion to pasture in the Waikato Region, New Zealand. Soil Use and Management. 18. 91-93.

Segers, R., 1998. Methane production and methane consumption: a review of processes underlying wetland methane fluxes. Biogeochemistry. 41. 23-51.

Shantz, M.A., Price, J.S., 2006. Hydrological changes following restoration of the Bois-des-Bel Peatland, Quebec, 1999-2002. Journal of Hydrology. 331. 543-553.

Sheppard, L.J., Crossley, A., Leith, I.D., Hargreaves, K.J., Carfrae, J.A., van Dijk, N., Cape, J.N., Sleep, D., Fowler, D., Raven, J.A., 2004. An automated wet deposition system to compare the effects of reduced and oxidised N on ombrotrophic bog species: Practical considerations. *Water, Air and Soil Pollution: Focus* 4. 197-205.

Silvola, J., Alm, J., Ahlholm, U., Nykanen, H., Martikainen, P.J. 1996. CO<sub>2</sub> fluxes from peat in boreal mires under varying temperature and moisture conditions. *Journal of Ecology*. 84. 219-228.

Smith, J.C., 2003. Fluxes of carbon dioxide and water vapour at a Waikato peat bog. Unpublished PhD thesis, University of Waikato. NZ.

Smith, L.C., MacDonald, G.M., Velichko, A.A., Beilman, D.W., Borisova, O.K., Frey, K.E., Kremenetski, K.V., Sheng, Y., 2004. Siberian peatlands a net carbon sink and global methane source since the early Holocene. *Science* 303, 353-356.

Sottocornola, M., Kiely, G., 2005. An Atlantic blanket bog is a modest CO<sub>2</sub> sink. *Geophysical Research letters*. 32. L23804.

Sottocornola, M. 2007 Four years of observations of carbon dioxide fluxes, water and energy budgets, and vegetation patterns in an Irish Atlantic blanket bog. Unpublished PhD thesis University College Cork.

Stewart, A.J.A., Lance, A.N. 1991. Effects of moor-draining on the hydrology and vegetation of northern Pennine blanket bog. *Journal of Applied Ecology*. 28. 1105-1117.

Stoneman, R. 1997. Peatland biodiversity - Introduction. In: Parkyn, L., Stoneman, R.E. & Ingram, H.A.P. (Eds.) *Conserving peatlands*. Guildford and King's Lynn, CAB International.

Strack, M. & Waddington, J. M. (2007) Response of peatland carbon dioxide and methane fluxes to a water table drawdown experiment. *Global Biogeochemical Cycles*, 21, GB1007, doi:10.1029/2006GB002715.

Strack, M. (Ed) 2008. *Peatlands and Climate Change*. International Peat Society, Finland.

Strack, M., Zuback, Y.C.A. 2013. Annual carbon balance of a peatland 10 yr following restoration. *Biogeosciences*. 10. 2885-2896.

Stroud, D.A., Reed, T.M., Pienkowski, M.W., Lindsay, R.A. 1988. *Birds, bogs and forestry. The peatlands of Caithness and Sutherland*. Ratcliffe, D.A., Oswald, P.H. (Eds). Nature Conservancy Council.

Suyker, A.E., Verma, S.B., Clement, R.J., Billesbach, D. P. 1996. Methane flux in a boreal fen: Season-long measurement by eddy correlation. *Journal of Geophysical Research- Atmospheres*. 101. 28637-28647.

Suyker, A. E., Verma, S. B. & Arkebauer, T. J. (1997) Season-long measurement of carbon dioxide exchange in a boreal fen. *Journal of Geophysical Research- Atmospheres*, 102, 29021-29028.

Tarnocai, C. 2009. The impact of climate change on Canadian peatlands. *Canadian Water Resources Journal*. 24 (4) 453-466.

Thompson, D.B.A., Macdonald, A.J., Marsden, J.H., Galbraith, C.A. 1995. Upland heather moorland in Great Britain - a review of international importance, vegetation change and some objectives for nature conservation. *Biological Conservation* 71(2): 163-178.

Thormann, M.N. 2006. Diversity and function of fungi in peatlands: A carbon cycling perspective. *Canadian Journal of Soil Science*. 86. 281-293.

Thuiller, W., Albert, C., Araujo, M.B., Berry, P.M., Cabeza, M., Guisan, A., Hickler, T., Midgely, G.F., Paterson, J., Schurr, F.M., Sykes, M.T., Zimmermann, N.E., 2008. Predicting global change impacts on plant species' distributions: Future challenges. *Perspectives in plant ecology evolution and systematic*. 9. 137-152.

Tuittila, E.-S., Komulainen, V.-M., Vasander, H., Nykanen, H., Martikainen, P. & Laine, J. 2000. Methane dynamics of a restored cut-away peatland. *Global Change Biology*. 6. 569-581.

Turunen, J., Tomppo, E., Tolonen, K., Reinikainen, A. (2002) Estimating carbon accumulation rates of undrained mires in Finland – application to boreal and subarctic regions. *Holocene*. 12. 69–80.

Turunen, J., Tolonen, K. 1996. Rate of Carbon accumulation in Boreal Peatlands and Climate Change. In: Lappalainen, E. (Ed.). *Global Peat Sources*. International Peat Society, Jyskä. 21-28.

Turunen, J., Roulet, N. T., Moore, T. R., Richard, P.J.H. 2004. Nitrogen deposition and increased carbon accumulation in ombrotrophic peatlands in eastern Canada. *Global Biogeochemical Cycles*. 18. 3.

UNECE 2010. Empirical critical loads and dose-response relationships. Expert workshop Noordwijkerhout 2010.

Van den bos, R. (2003). Restoration of former wetlands in the Netherlands; effect on the balance between CO<sub>2</sub> sink and CH<sub>4</sub> source. *Netherlands Journal of Geosciences*, 82, 325-332.

UNFCCC. 2001. Report of the conference of the parties on the second part of the sixth session, held at Bonn, 16<sup>th</sup> – 17<sup>th</sup> July 2001. FCCC/CP/2001/5, United Nations, Geneva.

Van der Wal, R., Pearce, I.S.K., Brooker, R.W. 2005. Mosses and the struggle for light in a nutrient-polluted world. *Oecologia*. 142. 159-168.

Van Wijk, M.T., Clemmensen, K.E., Shaver, G.R., Williams, M., Callaghans, T.V., Chapin III, F.S., Cornelissen, J.H.C., Gough, L., Hobbie, S.E., Jonasson, S., Lee, J.A., Michelsen, A., Press, M.C., Richardson, S.J., Rueth, H. 2003. Long-term ecosystem level experiments at Toolik Lake, Alaska, and at Abisko, Northern Sweden: generalizations and differences in ecosystems and plant type responses to global change. *Global Change Biology*. 10. 105-123.

Vitousek, P.M., Aber, J., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, G.D. 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological applications*. 7. 737-750.

Waddington, J.M., Warner, K.D., Kennedy, G.W. 2002. Cutover peatlands: a persistent source of atmospheric CO<sub>2</sub>. *Global Biogeochemical Cycles*. 16. 1-7.

Waddington, J.M., Roulet, N.T. 2000. Carbon balance of a boreal patterned peatland. *Global Change Biology*. 6. 87-97.

Walker, B.H., Steffen, W.L. 1997. The terrestrial biosphere and global change: Implications for natural and managed ecosystems. A synthesis of GCTE and related research. IGBP\_ICSU, Stockholm.

Wallage, Z.E., Holden, J., McDonald, A.T. 2006. Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. *Science of the Total Environment*. 367. 811-821.

Ward, S.E., Bardgett, R.E., Mcnamara, N.P., Adamson, J.K., Ostle, N.J., (2007). Long term consequences of grazing and burning on northern peatland carbon dynamics. *Ecosystems*. 10. 1069 – 1083.

Whitehead J.D., Twigg M., Famulari D., Nemitz E., Sutton M.A., Gallagher M.W., Fowler D. 2008. Evaluation of laser absorption spectroscopic techniques for Eddy covariance flux measurements of ammonia. *Environmental Science & Technology*. 42. 2041-2046.

Wiedermann, M.M., Gunnarsson, U., Ericson, L., Nordin, A. 2009. Ecophysiological adjustment of two *Sphagnum* species in response to anthropogenic nitrogen deposition. *New Phytologist*. 181. 208-217.

Wieder, R.K. & Vitt, D.H. (2006) Boreal peatland ecosystems, *Ecological Studies* 188, Springer, Berlin.

Williams, J.M. (ed.) 2006. Common Standards Monitoring for Designated Sites: First Six Year Report. Peterborough, JNCC.

Wille, C., Kutzbach, L., Sachs, T., Wagner, D., Pfeiffer, E. M. 2008. Methane emission from Siberian arctic polygonal tundra: eddy covariance measurements and modeling. *Global Change Biology*, 14, 1395-1408.

Wood E.C., Herndon S.C., Timko M.T., Yelvington P.E., Miake-Lye R.C. 2008. Speciation and chemical evolution of nitrogen oxides in aircraft exhaust near airports. *Environmental Science & Technology*. 42. 1884-1891.

Worrall, F., Reed, M., Warburton, J., Burt, T. 2003. Carbon budget for a British upland peat catchment. *The Science of the Total Environment*. 312. 133-146.

Worrall, F., Burt, T., Adamson, J. 2004. Can climate change explain increases in DOC flux from upland peat catchments? *Science of the Total Environment*. 326. 95-112.

Worrall, F., Armstrong, A. & Holden, J. (2007) Short-term impact of peat drain-blocking on water colour, dissolved organic carbon concentration, and water table depth. *Journal of Hydrology*, 337, 315-325.

Worrall, F., Burt, T.P., Rowson, J.G., Warburton, J., Adamson, J.K., 2009. The multi-annual carbon budget of a peat covered catchment. *Science of the total environment*. 407. 4084 – 4094.

Wu, Z., Dijkstra, P., Koch, G.W., Peñuelas, J., Hungate, B.A. 2011. Responses of terrestrial ecosystems to temperature and precipitation change: a meta-analysis of experimental manipulation. *Global change biology*. 17. 927-942.

Yamulki, S., Anderson, R., Peace, A., Morison, J.I.L. 2013. Soil CO<sub>2</sub> CH<sub>4</sub> and N<sub>2</sub>O fluxes from an afforested lowland raised peatbog in Scotland: implications for drainage and restoration. *Biogeosciences*. 10. 1051-1065.

Yiqi, L., Zhou, X. 2006. *Soil Respiration and the Environment*. Academic Press.

## 6.3 Appendix A

### 6.3.1 Tables associated with Chapter 3

Table 6.3.1. Exponential fitted line parameters for Whim Moss NEE fluxes ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) against PAR ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) using the following equation: Flux = A + B x ( $R^{\text{PAR}}$ ).

Plot	Dose ( $\text{kg N ha}^{-1} \text{y}^{-1}$ )	Form	A	B	R
2	8	Reduced	-3.652	3.763	0.997635
4	24	Oxidised	-4.127	4.6	0.997278
6	8	Oxidised	-6.003	6.385	0.99716
7	0	Control	-5.984	6.355	0.998634
9	24	Reduced	-4.645	5.128	0.997708
11	56	Oxidised	-7.009	7.413	0.998115
12	24	Oxidised	-5.924	6.223	0.998449
13	56	Oxidised	-5.034	5.802	0.997566
14	24	Reduced	-3.79	3.99	0.99864
16	0	Control	-8.59	8.87	0.999115
17	56	Reduced	-4.59	4.98	0.998619
18	24	Reduced	-40	40	0.999919
19	56	Reduced	-10.94	11.65	0.999385
20	24	Oxidised	-1.519	2.091	0.9979
21	56	Reduced	-5.67	6.21	0.998975
23	8	Reduced	-5.725	6.863	0.997562
25	56	Reduced	-3.36	3.46	0.998633
26	56	Oxidised	-7.87	8.15	0.999119
28	8	Oxidised	-3.598	3.639	0.99634
29	8	Oxidised	-7.26	7.408	0.998317
31	56	Oxidised	-4.664	5.652	0.996513
32	8	Oxidised	-14.67	15.21	0.999188
35	0	Control	-6	6.64	0.998374
36	8	Reduced	-5.963	6.326	0.998229
38	8	Reduced	-3.824	4.302	0.997448
40	0	Control	-4.48	4.85	0.999061
42	24	Reduced	-6.699	7.085	0.998481
43	24	Oxidised	-2.577	2.774	0.99255

Table 6.3.2. Multivariate regression for Whim Moss ecosystem respiration ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) against soil temperature ( $^{\circ}\text{C}$ ) and water table (cm) using the following equation: Flux = A + B x Soil T + C x WT depth.

Plot	Dose ( $\text{kg N ha}^{-1} \text{y}^{-1}$ )	Form	A (Constant)	B (Soil T multiplier)	C (Water table multiplier)
2	8	Reduced	-0.5870	0.0353	0.0412
4	24	Oxidised	0.5800	-0.2260	0.2090
6	8	Oxidised	0.1790	0.0037	0.2720
7	0	Control	-0.9800	-0.0460	0.2090
9	24	Reduced	-1.0000	0.0012	0.1090
11	56	Oxidised	-3.3800	-0.1790	0.5050
12	24	Oxidised	-1.8700	0.0306	0.1510
13	56	Oxidised	-0.4690	-0.2890	0.2400
14	24	Reduced	-0.3340	0.0216	0.0270
16	0	Control	-0.3740	-0.1240	0.0635
17	56	Reduced	-0.6660	0.0553	0.0376
18	24	Reduced	-0.0540	0.0033	0.0441
19	56	Reduced	-3.0400	-0.0625	0.2680
20	24	Oxidised	-0.7570	0.0640	0.0639
21	56	Reduced	-5.7700	0.8070	-0.0582
23	8	Reduced	-6.4200	1.0900	-0.2690
25	56	Reduced	0.7900	-0.2940	0.1900
26	56	Oxidised	-0.4100	0.0250	0.2150
28	8	Oxidised	-0.6650	0.1160	0.0039
29	8	Oxidised	-2.4500	0.4030	0.0181
31	56	Oxidised	4.6800	-0.7580	0.4610
32	8	Oxidised	-0.9010	0.2920	-0.0203
35	0	Control	-0.1500	-0.0470	0.0806
36	8	Reduced	4.0600	-0.6520	0.3130
38	8	Reduced	-3.8400	0.0262	0.2600
40	0	Control	0.4020	-0.0733	0.0774
42	24	Reduced	-1.4900	0.0736	0.0910
43	24	Oxidised	6.3600	-0.9400	0.3190

Table 6.3.3. Vegetation dry mass by species for individual plots at Whim Moss from plot vegetation harvesting.

Plot	N Dose Kg ha <sup>-1</sup> y <sup>-1</sup>	<i>Calluna vulgaris</i>		<i>Eriophorum vaginatum</i>	Mosses	<i>Sphagnum</i>	Moss & <i>Sphagnum</i>
		Wood (g)	Shoots (g)	(g)	(g)	(g)	(g)
2	8	60.65	54.1	10.92	152.48	0	0
4	24	56.16	48.74	5.21	126.94	0	0
6	8	84.04	89.65	26.77	30.6	15.27	0
7	0	57.83	33	21.26	95.94	0	0
9	24	73.6	57.28	1.77	188.24	0	0
11	56	33.35	56.15	7.47	85.47	0	0
12	24	58.23	62.24	7.22	61.53	0	0
13	56	95.25	72.18	6.51	178.9	0	0
14	24	23.54	34.93	1.69	160.6	0	0
16	0	23.06	25.24	25.38	0	217.39	0
17	56	62.5	48.79	0.68	75.26	83.26	0
18	24	51.09	28.12	3.48	146.27	0	0
19	56	64.03	40	36.17	116.49	0	0
20	24	66.06	12.28	1.75	144.31	0	0
21	56	55.87	57	31.67	76.36	0	0
23	8	51.73	77.48	46.35	220.53	0	0
25	56	22.38	16.41	42.74	0	0	79.18
26	56	42.68	67.38	16.11	195.64	0	0
28	8	24.33	26.32	22.92	0	205.51	0
29	8	67.13	101.41	7.74	171.36	0	0
31	56	236.08	146.64	18.28	133.08	0	0
32	8	113.83	115.66	17.45	0	0	185.35
35	0	96.44	40.86	49.7	90.79	0	0
36	8	106.41	72.34	19.76	133.02	0	0
38	8	78.83	59.86	16.74	102.36	0	0
40	0	38.74	51.86	9.43	81.31	97.24	0
42	24	69.49	61.27	28.47	162.53	0	0
43	24	108.3	53.5	14.09	101.98	0	0

Table 6.3.4. Whim Moss vegetation survey results for the most abundant species present.

Plot	N Dose Kg ha <sup>-1</sup> y <sup>-1</sup>	<i>Calluna vulgaris</i>			<i>Eriophorum vaginatum</i>		Mosses	Sphagnum
		% cover	Height (cm)	Shoot length (cm)	% cover	Height (cm)	% cover	% cover
2	8	75	36.7	28	10	39	100	0
4	24	50	31.3	16	10	38	100	0
6	8	90	47.3	20	45	60	10	75
7	0	60	39	18	55	46	0	0
9	24	45	35.3	11	5	33	75	25
11	56	90	30.4	12	10	53	100	0
12	24	100	40.8	20	10	50	100	0
13	56	75	39.3	10	10	29	100	0
14	24	40	29.8	7	0	0	5	85
16	0	45	26.4	13	50	48	0	100
17	56	50	44.8	4	3	0	20	80
18	24	30	36.5	6	10	37	100	0
19	56	80	31.6	6	50	30	80	0
20	24	45	48	15	3	0	65	0
21	56	50	29.4	7	85	42	10	0
23	8	85	34.4	14	80	31	5	0
25	56	10	64	3	90	39	5	10
26	56	90	21	7	10	32	100	0
28	8	25	29	6	35	42	0	100
29	8	100	50.2	13	15	41	100	0
31	56	180	48.6	17	35	39	80	0
32	8	120	36.8	10	5	49	5	95
35	0	60	40	12	80	55	100	15
36	8	70	33.6	8	30	40	100	0
38	8	90	37.8	10	10	32	100	0
40	0	30	28.5	7	1	30	10	60
42	24	40	34	11	50	48	80	0
43	24	35	46.5	3	15	32	30	0

## 6.3.2 Tables associated with Chapter 4

Table 6.3.5. Exponential fitted line parameters for Newbiggin NEE fluxes ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) against PAR ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) using the following equation: Flux = A + B x ( $R^{\text{PAR}}$ ).

Plot	Distance (m)	Treatment	Year 1			Year 2		
			R	B	A	R	B	A
1	5	Blocked	0.9822	0.3448	-0.0057	0.998995	1.409	-0.895
2	3	Blocked	0.998685	1.681	-1.402	0.997091	2.064	-1.304
3	1	Blocked	0.99771	0.306	-0.079	0.998956	1.669	-1.137
4	3	Blocked	0.946	0.3142	0.0087	0.99119	0.837	-0.016
5	5	Blocked	1.0005	-1.3	1.54	0.997763	1.924	-1.178
6	5	Control	0.999693	11.8	-11.4	0.998853	2.581	-1.861
7	3	Control	1.000666	-1.67	1.97	0.998045	2.031	-1.359
8	1	Control	0.99753	0.735	-0.421	0.998389	2.284	-1.677
9	3	Control	0.99338	0.903	-0.325	0.99683	0.598	-0.198
10	5	Control	0.903	0.4053	0.0199	0.99819	1.436	-1.167
11	5	Control	0.99583	0.776	-0.328	0.996734	1.648	-0.889
12	3	Control	0.999487	5.32	-4.79	0.996911	4.93	-3.496
13	1	Control	0.999729	20.68	-19.92	0.997197	4.572	-2.972
14	3	Control	0.99793	1.184	-0.874	0.999706	11	-10.3
15	5	Control	0.998019	3.343	-2.847	0.999431	14.1	-12.88
16	5	Blocked	0.999485	15.87	-14.99	0.997448	3.962	-2.958
17	3	Blocked	0.999285	5.61	-4.87	0.998137	4.13	-3.134
18	1	Blocked	0.999197	8.14	-7	0.99699	4.631	-3.41
19	3	Blocked	0.998128	6.963	-5.529	0.998228	4.528	-3.414
20	5	Blocked	0.998279	10.09	-8.974	0.99917	11.44	-10.38
21	5	Blocked	0.9994	5.34	-4.85	0.997839	2.834	-1.993
22	3	Blocked	0.997943	2.932	-2.417	0.998316	4.393	-3.127
23	1	Blocked	0.999195	5.277	-4.56	0.997723	5.779	-3.824
24	3	Blocked	1.000302	-4.1	4.35	0.998956	4.846	-3.646
25	5	Blocked	0.999643	6.73	-6.28	0.998223	4.656	-3.076
26	5	Control	0.99485	0.161	0.1272	0.998747	3.455	-2.364
27	3	Control	0.998611	1.817	-1.386	0.99337	0.555	0.156
28	1	Control	0.99975	3.85	-3.42	0.998423	7.054	-4.959
29	3	Control	1.00148	-1.019	1.656	0.997405	6.067	-4.291
30	5	Control	1.002469	-0.35	0.859	0.997288	2.468	-1.648

Table 6.3.6. Newbiggin CO<sub>2</sub> respiration regression fit parameters.

Plot	Distance (m)	Treatment	Year 1		Year 2	
			Constant	WT multiplier	Constant	WT multiplier
1	5	Blocked	-0.13	0.0519	0.01	0.0494
2	3	Blocked	-0.275	0.103	-2.83	0.321
3	1	Blocked	-0.281	0.0873	-0.899	0.159
4	3	Blocked	-0.236	0.084	0.281	0.0496
5	5	Blocked	-0.227	0.0843	0.328	0.0417
6	5	Control	-0.282	0.117	-0.516	0.111
7	3	Control	-0.226	0.0931	-0.193	0.102
8	1	Control	-0.159	0.0804	-0.728	0.143
9	3	Control	-0.186	0.0886	-1.08	0.145
10	5	Control	-0.213	0.0755	-0.309	0.063
11	5	Control	-0.312	0.143	0.005	0.086
12	3	Control	-0.365	0.152	-0.515	0.173
13	1	Control	-0.688	0.278	-0.214	0.163
14	3	Control	0.0117	0.00826	1.06	-0.0184
15	5	Control	0.201	-0.00246	0.216	0.0942
16	5	Blocked	0.095	0.00362	-1.8	0.329
17	3	Blocked	0.0257	0.00562	-3.38	0.523
18	1	Blocked	-0.409	0.241	-4.02	0.57
19	3	Blocked	-0.891	0.335	-3.02	0.484
20	5	Blocked	-0.331	0.121	-2.7	0.393
21	5	Blocked	-0.454	0.162	-2.83	0.366
22	3	Blocked	-0.353	0.132	-1.72	0.279
23	1	Blocked	-0.697	0.249	-3.37	0.493
24	3	Blocked	0.186	0.0102	-0.585	0.17
25	5	Blocked	-0.403	0.137	-0.007	0.146
26	5	Control	-0.138	0.103	-3.12	0.425
27	3	Control	-0.569	0.214	-1.66	0.233
28	1	Control	-0.266	0.126	-2.46	0.487
29	3	Control	-0.587	0.255	-1.39	0.326
30	5	Control	1.58	0.0044	-2.35	0.326

Table 6.3.7. Newbiggin CH<sub>4</sub> respiration regression fit parameters.

Plot	Distance (m)	Treatment	Year 1		Year 2	
			Constant	WT multiplier	Constant	WT multiplier
1	5	Blocked	-0.41	0.053	1.88	-0.047
2	3	Blocked	-0.33	-0.001	-1.86	0.297
3	1	Blocked	-0.36	0.074	-4.70	1.320
4	3	Blocked	1.32	-0.070	1.07	0.337
5	5	Blocked	0.56	0.014	-0.79	0.459
6	5	Control	1.97	-0.003	4.06	0.532
7	3	Control	3.52	0.104	5.54	0.062
8	1	Control	1.63	-0.068	0.56	-0.036
9	3	Control	0.53	0.104	1.41	0.618
10	5	Control	3.19	0.575	14.50	0.224
11	5	Control	2.95	-0.396	0.48	-0.001
12	3	Control	2.60	0.049	6.18	-0.016
13	1	Control	2.60	-0.070	-2.07	0.136
14	3	Control	5.20	0.110	10.40	3.410
15	5	Control	16.60	2.310	47.80	14.300
16	5	Blocked	7.03	0.774	38.20	-1.220
17	3	Blocked	0.98	-0.017	1.84	-0.072
18	1	Blocked	5.16	0.044	17.90	0.148
19	3	Blocked	11.60	0.461	43.40	0.788
20	5	Blocked	3.12	0.972	10.60	2.190
21	5	Blocked	6.73	-0.571	8.25	-0.207
22	3	Blocked	6.36	-0.082	15.00	-0.256
23	1	Blocked	9.27	0.200	29.20	0.531
24	3	Blocked	-0.62	0.399	1.87	0.106
25	5	Blocked	2.49	-0.252	4.01	-0.281
26	5	Control	1.77	-0.064	1.55	0.022
27	3	Control	1.81	-0.384	0.33	0.045
28	1	Control	9.33	-1.100	34.90	-2.420
29	3	Control	-1.54	0.062	2.54	2.060
30	5	Control	4.10	0.190	9.83	-0.480

Table 6.3.8. Newbiggin vegetation survey results for the most abundant species present

Plot	Distance (m)	N Dose Treatment	<i>Calluna vulgaris</i>			<i>Eriophorum vaginatum</i>		Mosses	Sphagnum
			% cover	Height (cm)	Shoot length (cm)	% cover	Height (cm)	% cover	% cover
1	5	Blocked	25	27.5	8	0	0	70	0
2	3	Blocked	50	30	8	0	0	100	0
3	1	Blocked	60	19.7	6.3	15	29	100	0
4	3	Blocked	50	7.3	5.7	0	0	100	0
5	5	Blocked	45	10	5.7	5	19	90	0
6	5	Control	25	14	3.5	10	18	0	85
7	3	Control	70	14.5	6	10	14	90	0
8	1	Control	85	18	6.3	10	20	90	0
9	3	Control	35	12.7	7	5	12	80	0
10	5	Control	25	6.3	3.7	40	18	0	30
11	5	Control	30	20	9	0	0	100	0
12	3	Control	65	23	12	0	0	100	0
13	1	Control	90	18.3	8	0	0	0	0
14	3	Control	10	10.7	3.7	80	22	40	60
15	5	Control	30	19.3	8.7	70	27	0	100
16	5	Blocked	30	19.5	6	40	21	0	100
17	3	Blocked	30	19	7	5	30	90	0
18	1	Blocked	60	18.8	7	15	24	0	70
19	3	Blocked	40	26.3	6	80	22	0	15
20	5	Blocked	40	24	10	70	26	0	80
21	5	Blocked	30	18	8	10	20	0	80
22	3	Blocked	45	20.3	8	15	23	0	80
23	1	Blocked	70	16.3	5	25	27	90	0
24	3	Blocked	60	20.8	7	0	0	50	0
25	5	Blocked	70	22	9	0	0	100	0
26	5	Control	40	22.3	9	0	0	65	0
27	3	Control	10	6.5	6.5	0	0	30	0
28	1	Control	45	22.5	9.7	5	20	100	0
29	3	Control	60	19.5	7	0	0	20	70
30	5	Control	60	20.3	9.3	15	32	5	10

Table 6.3.9. Mass of primary Newbiggin species by plot determined by use of equations 3.1 – 3.5 in conjunction with the vegetation survey carried out at the site.

Plot	Distance (m)	Treatment	Total <i>Calluna</i> (g m <sup>-2</sup> )	Green <i>Calluna</i> (g m <sup>-2</sup> )	<i>Eriphorum</i> (g m <sup>-2</sup> )	Moss & Sphagnum (g m <sup>-2</sup> )	All vegetation (g m <sup>-2</sup> )
1	5	Blocked	383.3	221.0		1072.7	1676.9
2	3	Blocked	715.0	375.7		1167.7	2258.4
3	1	Blocked	715.5	447.8	100.6	1167.7	2431.6
4	3	Blocked	449.4	389.5		1167.7	2006.6
5	5	Blocked	420.5	358.5	68.8	1136.0	1983.9
6	5	Control	225.3	247.9	86.5	1120.2	1679.8
7	3	Control	775.7	511.5	87.6	1136.0	2510.8
8	1	Control	998.1	602.5	85.9	1136.0	2822.6
9	3	Control	331.1	288.9	70.9	1104.4	1795.2
10	5	Control	135.2	246.7	190.6	946.0	1518.5
11	5	Control	356.0	246.0		1167.7	1769.7
12	3	Control	814.6	444.7		1167.7	2427.0
13	1	Control	1062.1	623.3			1685.5
14	3	Control	5.2	153.8	328.2	1167.7	1654.9
15	5	Control	347.8	247.8	292.1	1167.7	2055.3
16	5	Blocked	350.2	263.9	189.7	1167.7	1971.4
17	3	Blocked	344.3	257.9	65.7	1136.0	1803.9
18	1	Blocked	705.0	443.6	102.1	1072.7	2323.3
19	3	Blocked	550.7	325.8	328.2	898.5	2103.2
20	5	Blocked	523.8	301.9	292.4	1104.4	2222.4
21	5	Blocked	332.6	251.9	85.9	1104.4	1774.8
22	3	Blocked	541.0	344.8	102.4	1104.4	2092.5
23	1	Blocked	796.7	517.5	135.9	1136.0	2586.1
24	3	Blocked	728.4	443.6		1009.3	2181.3
25	5	Blocked	863.4	493.6		1167.7	2524.7
26	5	Control	503.9	307.9		1056.9	1868.6
27	3	Control	-44.0	137.1		946.0	1039.2
28	1	Control	566.8	334.6	68.6	1167.7	2137.6
29	3	Control	713.2	443.6		1136.0	2292.8
30	5	Control	722.5	429.9		898.5	2050.9

Table 6.3.10. Leaf area index for primary species at Newbiggin calculated using equations 3.6 and 3.7.

Plot	<i>Calluna</i> LAI	<i>Eriphorum</i> LAI	Moss & Sphagnum LAI	All vegetation LAI
1	0.80		0.70	1.50
2	1.50		0.81	2.31
3	1.50	0.30	0.81	2.61
4	0.94		0.81	1.75
5	0.88	0.24	0.77	1.90
6	0.47	0.27	0.75	1.50
7	1.63	0.27	0.77	2.68
8	2.10	0.27	0.77	3.14
9	0.69	0.24	0.73	1.67
10	0.28	0.46	0.54	1.29
11	0.75		0.81	1.56
12	1.71		0.81	2.52
13	2.23			2.23
14	0.01	0.71	0.81	1.53
15	0.73	0.64	0.81	2.18
16	0.74	0.46	0.81	2.00
17	0.72	0.24	0.77	1.73
18	1.48	0.30	0.70	2.48
19	1.16	0.71	0.49	2.35
20	1.10	0.64	0.73	2.48
21	0.70	0.27	0.73	1.70
22	1.14	0.30	0.73	2.17
23	1.67	0.36	0.77	2.81
24	1.53		0.62	2.15
25	1.81		0.81	2.62
26	1.06		0.68	1.73
27	-0.09		0.54	0.45
28	1.19	0.24	0.81	2.24
29	1.50		0.77	2.27
30	1.52		0.49	2.00

### 6.3.3 Tables associated with Chapter 5

Table 6.3.11. Forsinard methane flux regression fit parameters.

Plot	Constant	Multiplier
1	8.63	-0.408
2	34.30	-1.87
3	1.32	0.093
4	25.50	0.49
5	1.50	1.07
6	4.50	0.62
7	20.00	-0.26
8	1.15	-0.0601
9	2.10	3.41
10	3.09	0.487
11	4.02	-0.245
12	0.05	0.0046
13	7.00	0.24
14	4.40	0.584
15	32.30	-0.63
16	11.80	0.51
17	2.07	0.142
18	5.50	2.18
19	-5.10	2.37
20	5.90	1.55

