Carbon fluxes at an upland blanket bog in the north Pennines

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Andrew Richard Lloyd

B.Sc. (Hons), M.Sc.

Department of Biological and Biomedical Sciences

Durham University

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Declaration

The material contained within this thesis has not previously been submitted for a degree at Durham University or any other university. The research reported within this thesis has been conducted by the author unless indicated otherwise.

Andrew Richard Lloyd
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Abstract

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The peat soils found in blanket bogs are significant stores of carbon. The degree to which these ecosystems are currently functioning as sinks or sources of carbon is not clear. There is a paucity of measurements from suitable sites but the available evidence suggests that certain sites might be close to being carbon neutral or acting as a net source of carbon to the atmosphere. A complete understanding of the carbon budget of a landscape requires a comprehensive assessment of the magnitude of the whole range of pathways by which carbon enters and leaves the system.

Measurements were made of all of the key gaseous carbon fluxes, including the net CO_2 flux, the soil CO_2 flux and emissions as methane. A flux partitioning model was utilised to separate the net CO_2 flux into its component parts. Values for the fluvial carbon losses from the site were taken from the literature. The various CO_2 fluxes were by far the largest terms in the complete carbon budget. Growing season measurements showed that methane emissions were a small component.

The key environmental variables that were driving the temporal variations in the fluxes were identified. In general soil temperature was important in explaining variations in ecosystem respiration, soil CO_2 fluxes and the methane flux. The water table was usually high and fluctuations did not appear to affect carbon fluxes. There was evidence of increased soil CO_2 fluxes as a response to low soil moisture levels during a summer dry period.

A comprehensive carbon budget for the blanket bog at Moor House NNR showed the site to be a relatively large carbon sink, of an estimated 134.09 ± 32 g C m^{-2} yr^{-1}.

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CHAPTER 1

INTRODUCTION AND AIMS

1.1 Introduction

Peatlands are significant stores of carbon and can be significant sinks of carbon. The balance of the many carbon pathways involving a wide variety of different organisms will determine whether a particular peatland is behaving as a net carbon sink or a net source of carbon to the atmosphere. Northern peatlands may cover only 3 % of the earth's land area (Maltby and Immirzi, 1993), but they are estimated to store in the region of 30 % of the global soil carbon (Gorham, 1991). It is these factors that make peatlands a significant component of the global carbon cycle and the subject of an intensive research effort over the last 20 years.

The majority of the pathways in the peatland carbon cycle are common to most other terrestrial ecosystems; what makes peatlands unique are the tendencies for processes to have different rates and for there to be differences in the relative size of the flux pathways. Peatlands develop when carbon sequestered into the vegetation and soils as organic matter fails to be balanced by the release of carbon to the atmosphere through respiration and decomposition (Blodau, 2002). A range of environmental factors combine to produce the waterlogged and anoxic conditions which suppress the rate of respiration and decomposition and layers of organic matter begin to accumulate forming peat (Charman, 2002). The major input of carbon into the system is through gross primary productivity (GPP) or photosynthesis, while carbon may be lost from the system as plant and soil respiration, methane (CH_4) emissions and the fluvial fluxes of dissolved and particulate organic carbon (DOC and POC). The balance of the carbon flux contained within each of these pathways will determine the carbon balance of an area of peat. The magnitude of each of the fluxes is controlled by a complex set of interacting biological, chemical and physical factors and fluxes are highly variable at a range of spatial and temporal scales (Humphreys *et al.*, 2006). In general temperature and water table have been shown to explain much of the seasonal, annual and interannual variations that control whether a peatland is a net sink or source of carbon. This fact has been widely noted in experimental and field studies (Moore and Knowles, 1989, Moore and Dalva, 1993, Blodau and Moore, 2003, Lafleur *et al.*, 2003) and there are obvious links with predicted changes in these environmental variables over the coming decades due to climate change (IPCC, 2007). This has raised the possibility of potentially significant positive feedback loops, whereby changes in climate, particularly at northern latitudes promote an increase in the release of important greenhouse gases from northern peatlands (Gorham, 1991, Bridgham *et al.*, 1995, Ise *et al.*, 2008). However, the exact and relative roles that these climatic and environmental variables play in controlling carbon fluxes remains a subject of continued research (Bubier *et al.*, 2005, Lafleur *et al.*, 2005, Mäkiranta *et al.*, 2009). There is a requirement for greater understanding of these responses which will eventually be implemented into new land surface models. This will provide the opportunity for improved representation of these processes and potential feedback mechanisms within global climate models (Cox *et al.*, 2000).

The term 'blanket bog' refers to a particular type of ombrotrophic, or 'rain-fed', peatland which exhibits a globally restricted distribution but is extensively found in the British Isles, where the cool, wet, oceanic climate provides the required conditions for peat formation. These blanket bogs have received relatively little attention in terms of carbon-cycling research in recent years compared to the well studied continental bogs found in the boreal and arctic zones (Fowler *et al.*, 1995, MacDonald *et al.*, 1998, Laine *et al.*, 2007). In Scandinavia and North America, for example, studies are more advanced with several long-term records of continuous carbon flux measurements in existence (Aurela *et al.*, 2002, Lafleur *et al.*, 2003, Sagerfors *et al.*, 2008). Despite the importance of these ecosystems in terms of carbon storage and as habitats for biodiversity, much of the blanket bog in the UK is believed to be in poor condition (Holden *et al.*, 2007). Factors such as over-grazing, forestry plantation, pollution, erosion, heather burning and the digging of drainage ditches during the last century has meant that many areas of blanket bog may not be functioning as 'active' peat (Ramchunder *et al.*, 2009). Such processes have been shown to cause reduced carbon storage and promote the loss of carbon from the system (Garnett *et al.*, 2000, Ward *et al.*, 2007, Clay *et al.*, 2009). Within recent years, there has been an acknowledgment of the bad practice and attempts are being made to restore and conserve large areas of upland blanket bog (Wallage *et al.*, 2006, Armstrong *et al.*, 2009). A great deal of public money is being invested in projects to change the management of these areas with the aim of returning them to 'healthy' functioning peatlands (Moors for the Future Partnership, 2008). Suggestions have even been made that landowners could be awarded 'carbon credits' as a reward for restoring areas of peatland (National Assembly for Wales, 2009). Despite these investments, there have been relatively few studies that have quantified the complete carbon budget of ‘good condition’ blanket bog (Billett *et al.*, 2004). An accurate quantification of the carbon balance of good quality, active blanket bog is essential as restoration programmes seek to return areas of degraded bog to such conditions. Some progress has been made by Worrall and colleagues at Moor House – Upper Teesdale National Nature Reserve in the North Pennines (Worrall *et al.*, 2003, Worrall *et al.*, 2009). The blanket bog at Moor House can be termed ‘pristine’, with low levels of active land management and the carbon balance of such a site will likely be regarded as a best case scenario in terms of carbon sequestration rates. Despite the work to date, while there are good estimates for the fluvial fluxes of carbon from the area, the budgets have lacked site specific data for the gaseous carbon fluxes of carbon dioxide (CO_2) and methane.

1.2 Aims

This project aims to provide improved understanding of the gaseous carbon fluxes at an upland blanket bog in the north Pennines. The magnitude of the fluxes of CO_2 and methane between the land surface and the atmosphere will constitute some of the largest and most important terms in a complete carbon budget for blanket bog. Consideration of these fluxes together with estimates of the fluvial fluxes from the existing literature will allow a new assessment of carbon balance of this ecosystem. Individual components of the gaseous carbon flux will be considered separately and in turn, in order to determine the key driving variables that are controlling how much carbon is being sequestered through photosynthesis and how much is being returned to the atmosphere through ecosystem respiration, soil respiration and methane emissions. The broad aims of the project are to answer these questions:

- What is the net flux of gaseous CO_2 between the atmosphere and land surface? and what are the relative roles of its component fluxes of primary productivity and ecosystem respiration?

- Does the standard technique of inserting measurement collars into the soil affect our interpretation of the measured soil CO_2 flux?

- How much carbon is respired from the peat? and which factors control the process?

- How important is the flux of methane in determining the carbon balance? and which environmental factors control the flux?

1.3 Plan of the thesis

This first chapter has aimed to briefly introduce the subject area of peatland science and carbon cycling. In light of that discussion, the aims and scope of the remainder of the thesis are outlined.

Chapter two includes a detailed review of the literature relevant to the work presented in the subsequent chapters. The study area at Moor House – Upper Teesdale National Nature Reserve is introduced. The site has a long history of past research which is relevant to today's interest in carbon cycling and this is briefly reviewed.

Chapter three presents the gaseous CO_2 balance of an area of upland blanket bog in the northern Pennines. The method of data collection and processing using the eddy covariance technique is described. The net CO_2 flux is partitioned into gross primary productivity and ecosystem respiration; relationships between the fluxes and environmental variables are established and these are used to develop a gap-filling routine.

In chapter four the focus moves to studying a component of the net CO_2 flux. Soil CO_2 fluxes are commonly measured using chamber techniques, the hypothesis that inserting measurement collars into the soil has a significant effect on the measurements is tested.

Chapter five draws on the methodological developments from chapter four to provide high temporal resolution measurements of soil CO_2 fluxes over a period of eight months. Spatial variation in the magnitude of the fluxes is examined and the hypothesis that vegetation type has a significant effect on the magnitude of the soil CO_2 flux is tested. The controlling variables are identified and models are developed to allow an estimate of the annual contribution of soil respiration to the net CO_2 flux measured in chapter three.

The previous three chapters have addressed the magnitude and controls on CO_2 fluxes at the site, in this penultimate chapter, the focus moves to another potentially important carbon flux, namely methane. Campaign measurements of methane fluxes were made using the eddy covariance and closed chamber techniques and an estimate of the seasonal methane flux is presented.

Finally chapter seven provides a brief overview the findings from the thesis as a whole. The results are discussed in relation to each other and the published literature. In light of this work, a new and more complete carbon balance for the site is presented. Areas of further work based on these findings are highlighted.

CHAPTER 2

BACKGROUND TO PEATLAND CARBON CYCLING AND MOOR HOUSE NNR

2.1 Introduction

Some of the issues relevant to the topic of carbon cycling in peatlands were briefly introduced in Chapter 1. This chapter discusses the stores and fluxes of carbon in greater detail; the relevant scientific literature is reviewed, the existing state of knowledge is presented and gaps in our present understanding are highlighted. The chapter begins with a review of relevant experimental techniques which have been used to collect the data described later in the chapter and are relevant to the methods used in the subsequent chapters of this thesis.

2.2 Methods used to study carbon fluxes in the field

There are a range of tools and techniques available to those studying soil-surface carbon fluxes. The results of studies using these methods in a variety of ecosystems are widely reported in the literature. However, each approach has problems or at least assumptions and prerequisites that must be met, meaning that there is no one ideal system for all situations (Fox *et al.*, 2008; Janssens *et al.*, 2001; Norman *et al.*, 1997). There have also been a number of useful studies comparing results obtained using the different methods (Norman *et al.*, 1997; Reth *et al.*, 2005; Schulze *et al.*, 2002). In the following section these techniques will be discussed along with their potential advantages and disadvantages.

2.2.1 Eddy covariance

Eddy covariance (EC) has become the most widely used method of studying net CO_2 (as well as H_2O and sensible heat) fluxes between terrestrial ecosystems and the atmosphere. This is largely due to its adoption as the standard protocol by large international consortia such as CARBOEUROPE and Ameriflux, involving over 200 study sites worldwide (Aubinet *et al.*, 2000; Olson *et al.*, 2004). The atmosphere contains turbulent motions of upward and downward moving air, called eddies, that transport trace gases across the canopy-atmosphere interface (Baldocci, 2003). The eddy covariance technique samples these eddies for their vertical velocity and concentration of gases (e.g. CO_2, H_2O and CH_4). Statistical analysis is used to average the recorded fluctuations in concentrations over a time period of usually 30 minutes, which gives a value of the net amount of material being transported vertically between the surface and atmosphere (Aubinet *et al.*, 2000; Baldocci, 2003).

Baldocchi (2003) identifies a number of factors that account for the popularity of the eddy covariance technique:

1. It is a scale-appropriate method, providing ecosystem scientists with a measure of net CO_2 exchange for a whole ecosystem.
2. It is a direct measurement of net CO_2 exchange across the canopy-atmosphere interface, an important component of carbon cycling.
3. The area sampled (the flux footprint) can be large and can be altered to suit the location.
4. The technique can calculate fluxes over hourly periods or can be maintained for years to allow the calculation of annual ecosystem fluxes.
5. As well as simply calculating carbon fluxes for an area, the longer-term systems can be used to study ecosystem responses to environmental perturbations.
6. An added advantage of eddy covariance compared to traditional chamber methods is that the act of measuring does not affect the emission of gases from the soil (Norman *et al.*, 1997).

However, the theory behind the eddy covariance method dictates that there are a number of assumptions that should be met. Ideally the eddy flux tower should be sited over a flat area, where the environmental variables are steady, the vegetation being studied is homogeneous, especially in the upwind direction, and there is no advection (Baldocchi, 2003). During stable conditions, such as calm nights, these assumptions may not be met and consequently, extensive and complex quality checks must be carried out to identify and discard poor-quality data, which would otherwise cause systematic errors in the calculation of the fluxes (Goulden *et al.*, 1996; Reth *et al.*, 2005). This necessary practice, together with problems of instrument break-down, means that there will inevitably be gaps in long-term data records that must be filled if producing seasonal or annual flux measurements (Baldocchi, 2003). For small gaps of a few hours simple interpolation between adjacent periods may be sufficient (Baldocchi, 2003). For longer gaps a time-dependent mean, calculated over a two week period, can be used to replace absent data (Moncrieff *et al.*, 1996). A more complex approach relies on filling gaps using empirically-derived algorithms that are calculated using variables such as temperature. However, the relationships change depending on the time of year and so require continual updating (Aubinet *et al.*, 2000; Baldocchi, 2003).

Eddy covariance yields highly useful values of net ecosystem exchange (NEE) but it can also be desirable to have an understanding of its two major components: gross primary productivity (GPP) and ecosystem respiration (ER). A ‘flux-partitioning algorithm’ can be used to produce estimates of the two components. This operates by extrapolating the known night-time values of ecosystem respiration into the daytime, traditionally a temperature response function derived from long-term data sets is used. However in a recent paper, Reichstein *et al.* (2005) showed that using a temperature sensitivity value derived from long-term (annual) data to extrapolate over short-term periods (night to day) introduces significant biases because annual data are confounded by seasonal effects. They suggest and recommend a new algorithm that defines a short-term sensitivity of ER to temperature, which is more appropriate when extrapolating from night to daytime. The authors point out that there are situations when flux partitioning benefits from independent methods of estimating the short-term sensitivity of ER to temperature, which can be achieved using soil respiration chambers (Reichstein *et al.*, 2005).

2.2.2 Chamber methods

Chamber-based methods are most frequently used to estimate soil CO_2 fluxes, being relatively inexpensive and easy to use (Janssens *et al.*, 2001; Norman *et al.*, 1997; Pumpanen *et al.*, 2004). Norman *et al.* (1997) recognise three widely used chamber systems that operate using different principles:

1. In closed-dynamic systems air is circulated between the chamber and an external IRGA, the chamber is closed for a period of typically less than five minutes, during which time the IRGA is continuously sampling and measuring CO_2 concentrations. The change in concentration in the chamber over time is proportional to the soil CO_2 flux (Norman *et al.*, 1997). In this system chamber effects such as pressure anomalies can be minimized by the addition of new vent designs as in the LI-8100, that allow chamber pressure to track ambient pressure under calm and windy conditions (McDermitt *et al.*, 2005). Further advantages

arise from the short sampling time, limiting the time that the chamber is affecting the soil and allowing greater spatial sampling. In automated systems greater temporal sampling is also possible.

2. Some larger chambers have been used with the closed-static method (Crill, 1991). Chambers are manually placed on collars in the ground (typically for a period of 30 minutes) and three to four gas samples are obtained periodically with syringes, samples are then analyzed using gas chromatography in the laboratory. A small fan may be used to provide adequate mixing and flux estimates are based on changes in CO_2 concentrations in the chamber. Norman *et al.* (1997) showed that closed-static chambers can seriously underestimate surface fluxes; as CO_2 concentrations in the chamber increase over the relatively long 30 minute period, the rate of gas diffusion from the soil slows to unnaturally low levels. However the method does allow the fluxes of multiple gases to be estimated simultaneously (Norman *et al.*, 1997). In addition, the use of larger chambers reduces the problems of failing to sample fine scale spatial variability.

3. In open-chamber techniques, a continuous stream of air is passed through the chamber and fluxes are calculated based upon the difference in concentrations between incoming and outgoing air (Subke & Tenhunen, 2004). Open systems can suffer from significant flux errors due to pressure anomalies caused by the flow of air through the chamber. There are methods to minimise these problems (Norman *et al.*, 1997) meaning that it can be an accurate way of obtaining continuous flux measurements.

NEE chambers (which cover vegetation as well as soil) are also available that take into account fluxes due to photosynthesis as well as plant and soil respiration, therefore measuring the same fluxes as eddy covariance. The ability to manipulate conditions inside the chamber (by changing light levels) allows the experimental separation of fluxes due to photosynthesis and respiration, a clear advantage over eddy covariance. However, the method is labour-intensive, cannot be used for continuous monitoring and suffers from the usual problem of ‘chamber effects’.

A final chamber technique combines closed-static chambers with chemical traps such as soda lime that fix released CO_2. Norman *et al.* (1997) however excluded it from their comparison of techniques on the basis that it had been shown to be too unreliable, underestimating fluxes by 10 to 100 %.

2.2.2.1 Experimental use of chambers

Chamber systems can be manual, where a person is required to place the chamber on the soil and be present for the measurement or automated where the chamber can close, take a measurement and open again, all automatically. Generally the choice between which system to use involves a trade-off. Manual systems can achieve greater spatial distribution as the chamber can be moved around many plots, however this is labour-intensive and so has a poorer temporal resolution (Savage & Davidson, 2003). Automated systems require as many chambers as plots and so there is usually less spatial distribution, however measurements can be taken every hour (Savage & Davidson, 2003). Savage and Davidson (2005) compared soil respiration measurement made with a manual system to those made with an automated system at a single forest site. Manual measurements were taken at 12 plots once a week during the morning, while automated measurements were taken every hour at just three plots. While measurements made during the same hour showed that the two systems agreed well with each other, the manual system had a smaller standard deviation and so increased the confidence of the estimate. When manual measurements were extrapolated, they consistently underestimated the daily flux compared to the continuously monitoring auto-system. However, over a two month period the two systems again showed a good agreement. Because of this the authors conclude that a spatially well distributed manual system may be the best approach when a simple estimate of seasonal soil respiration is the objective. In cases where short-term responses to soil moisture and temperature variation are being studied or modelled, then the higher temporal resolution of the auto-system will be preferable. Additionally the authors suggest that frequent measurements may be particularly important if soil respiration is being measured alongside eddy covariance estimates of net ecosystem exchange (Savage & Davidson, 2003). Finally, Savage and Davidson (2003) conclude that ideally a study would combine both systems, providing estimates that were of a high temporal frequency and distributed over a larger area. The “LI-8100 Automated Soil CO_2 Flux System” manufactured by LI-COR (LI-

COR, 2005), with both automated and manual survey chambers is ideal for the experimental design recommended by Savage and Davidson (2003). In a further improvement to this design, LI-COR and the Centre for Terrestrial Carbon Dynamics (CTCD) have designed and built a multiplexed automated soil respiration system with 12 auto-chambers linked to a single IRGA (CTCD, 2005). This system combines the benefits of continuously monitoring chambers with a much greater degree of spatial coverage.

2.2.2.2 The effects of collar insertion

All chamber techniques require a collar of some sort to be inserted into or to lie on the soil surface, serving as a seal and an anchor for the chamber. However, using a collar could be another way in which chamber techniques alter the soil environment that they are measuring. Inserting collars into the soil will cut through plant roots, and as root respiration can be significant (up to 40-60 % of total soil respiration) this could be a large source of error (Hanson *et al.*, 2000). Wang *et al.* (2005) investigated the effects of inserting collars on soil respiration measurements in a larch forest. They showed that soil respiration rates were affected by the depth the collar used; specifically rates were significantly lower for 5cm and 8cm collar depths compared to 0.3cm and 2 cm collars. Wang *et al.* (2005) conclude that the root cutting effect should be taken into account when measuring soil respiration using collars and chambers. Obviously the size of the effect will depend on the collar depth that is being used as well as the root physiology of the plants.

2.2.3 Combined studies using EC and chambers

A number of studies have been published that either compared eddy covariance with chamber measurements (Fox *et al.*, 2008; Norman *et al.*, 1997; Reth *et al.*, 2005) or developed methodologies of combining the techniques to quantify ecosystem carbon fluxes (Reth *et al.*, 2005; Wohlfahrt *et al.*, 2005).

In comparisons, CO_2 fluxes estimated by eddy covariance have been shown to be 30-50 % less than those estimated using chamber methods (Reth *et al.*, 2005). Many of these studies were carried out at forest sites comparing below-canopy eddy covariance measurements to soil respiration chambers. There are several explanations for these discrepancies; firstly the two measurement techniques measure fluxes from different areas, from a maximum of 1 m^2 with chambers to a very much larger and variable area with EC (Reth *et al.*, 2005). A second and related reason is that the techniques are measuring different processes. In a forest under-storey Janssens *et al.* (2001) observed a diurnal pattern in eddy fluxes that was absent from the chamber-derived fluxes. Whilst the chambers were measuring purely soil fluxes, the eddy fluxes included photosynthesis from the moss under-storey (Janssens *et al.*, 2001). Similarly in a moorland ecosystem, EC measurements would include substantial influences from photosynthesis, which would not be accounted for using soil chambers.

More direct comparisons showed night-time ER (derived from NEE chambers) exceeded night-time EC fluxes by 10-35 % in a meadow (Wohlfahrt *et al.*, 2005), by 20-40 % in six boreal forests (Lavigne *et al.*, 1997) and by 35 % in a deciduous forest (Goulden *et al.*, 1996). Wohlfahrt *et al.* (2005) attributed the difference to errors associated with the chamber technique and the different measurement scales. However, Lavigne *et al.* (1997) believed that although there may have been some errors in up scaling the chamber measurements, the discrepancies were primarily due to underestimates in the EC measurements. There is some uncertainty as to which method provides the most accurate estimate of ecosystem respiration, which is clearly a problem; in particular we should be cautious when making intercomparisons between sites when different methods have been used.

One integrated study on northern Canadian wetlands used colour air photography to divide a large area into ‘microtopographical elements’. Chamber measurements taken in the different areas were then upscaled to produce a spatially-weighted average of methane fluxes for the whole site (Roulet *et al.*, 1994). The estimated fluxes derived using the modelled chamber data were found to compare well with eddy covariance flux measurements made over the same site and during the same summer month (Edwards *et al.*, 1994; Roulet *et al.*, 1994). Earth observation data were used to explore further the flux measurements made by eddy covariance at heights of 5m and 18m. The fetch at 18m in particular was heterogeneous, including larger fractions of wet areas and ponds. The flux footprint was modelled and divided up into wind direction intervals and an earth observation product (LANDSAT-TM) was used to estimate the fraction of wet areas within each wind direction sector. It is important to note that only a coarse estimate was possible as the LANDSAT-TM has a pixel size of 30 × 30m, while many of the different landscape features were at a smaller scale. Nevertheless, the authors were able to show a strong relationship between methane flux and the percentage of wet areas in a sector (Edwards *et al.*, 1994). This study is an example of where earth observation data were used to scale up chamber measurements to give an estimate of landscape fluxes. Furthermore the satellite imagery was able to show relationships between the physical characteristics of the landscape and variable flux measurements.

2.2.4 Measurements during snow cover

Winter measurements of carbon dynamics are relatively rare, largely because of the practical and logistical difficulties of taking measurements in the inhospitable climates of the northern winter. Over half of northern ecosystems are snow covered for most of the year, in the past many trace gas budgets were calculated on the basis of summer-time measurements with the assumption being that fluxes ceased when temperatures dropped below 0°C or the surface became snow covered (Sommerfeld *et al.*, 1993). However more recently studies have shown that winter-time fluxes from under snow-cover can represent an important part of the annual carbon budget (Brooks *et al.*, 1997; Bubier *et al.*, 2002; Hirano, 2005; Lafleur *et al.*, 2001; Sommerfeld *et al.*, 1993). Eddy covariance has successfully been used over the winter months at a few sites to demonstrate the importance of winter-time NEE (Lafleur *et al.*, 2001). The use of chamber methods is very rare, presumably because of the technical difficulties; automatic chambers need to be fully opening to allow normal snow cover and high enough to leave air in the head-space above the snow. One such system (closed-dynamic chambers) was developed by Bubier *et al.* (2002) to measure continuously NEE over a temperate peatland throughout the winter. Nykänen *et al.* (1995) used manual closed chambers, but removed the snow and placed the chamber against the frozen soil. In removing the snow, the natural conditions were clearly being altered and it seems likely that the fluxes they measured will be different from the actual rates of CO_2 diffusion through the snow. Mariko *et al.* (2000) found that simply placing manual chambers (with an open-flow IRGA) on the snow surface to measure fluxes performed well compared to other methods. However, others have questioned the effect of disturbing the snow surfaces by installing chambers (Hirano, 2005). The other main technique that has been used is the flux gradient method (Brooks *et al.*, 1997; Hirano, 2005; Risk *et al.*, 2002; Sommerfeld *et al.*, 1993). This involves measuring CO_2 concentration gradients through the snowpack and using Fick's first law of diffusion to calculate the gas flux to the surface. The equation requires an estimate of the gaseous diffusion coefficient through the snowpack, which can be difficult to determine (Hirano, 2005). Commonly, gas collectors are installed in the soil and at intervals in the snowpack, gas samples are then removed using syringes and analysed using gas chromatography (Brooks *et al.*, 1997; Sommerfeld *et al.*, 1993).

2.3 *Carbon dynamics in peatland ecosystems*

2.3.1 Gaseous CO_2 fluxes

Most peatlands are considered to be sinks for carbon because in most cases the input of CO_2 by photosynthesis exceeds that respired by vegetation, soil animals and microorganisms (Charman, 2002). The rate of net primary productivity (NPP) will control the input of carbon. Estimates of NPP vary hugely, values of between 100 – 400 g m^{-2} yr^{-1} are most common, putting peatland productivity at a similar level to boreal forests (Blodau, 2002; Moore *et al.*, 2002). However, importantly this excludes below-ground productivity, which can be considerable, often exceeding 300 g m^{-2} yr^{-1} (Charman, 2002; Moore *et al.*, 2002). The variation in estimates is probably due to actual variability between and within peatlands. Higher water tables, temperatures and in some cases increased nitrogen may increase NPP. In short-term studies, elevated CO_2 concentrations have also been shown to increase NPP in *Sphagnum* mosses (Blodau, 2002).

CO_2 is released from peatlands by respiration and mineralization of organic carbon by microbial decomposition (Blodau, 2002). Compared to other ecosystems, carbon mineralization is slow and dependent upon oxygen availability, microbial activity, temperature and vegetation type. The majority of the CO_2 released from peatlands is a result of aerobic decay within the surface layers that lie above the water table. The production rate of CO_2 in peat soils is temperature dependent, increasing by 2-3 times for a 10°C increase in temperature (Lavigne *et al.*, 1997; Moore & Dalva, 1993). Much more variable Q_{10} values have also been recorded and according to Blodau (2002) the mechanism underlying the temperature effect on CO_2 production is unclear.

Because peatlands are typically waterlogged or have high water tables for large parts of the year, relatively small sections of the peat column are able to support aerobic decomposition. Freeman *et al.* (2001b) have suggested that low decomposition rates in the catotelm are due to a lack of oxygen constraining a single enzyme, phenol oxidase. Under limited phenol oxidase activity, phenolic compounds are able to accumulate which then inhibit other important decomposing extra-cellular enzymes (Freeman *et al.*, 2001b; Freeman *et al.*, 2004b). There is an element of anaerobic decay that occurs in the catotelm, releasing some CO_2, although the process is a thousand times slower than aerobic decay (Belyea & Clymo, 2001). Finally the microbial oxidation of methane produced in the anaerobic zone will be a minor source of CO_2 (Charman, 2002). The exact interrelationships between these variables and carbon mineralization are complex, but overall, higher temperatures and lower and fluctuating water tables are associated with increased mineralization (Blodau, 2002; Blodau & Moore, 2003). Research has shown that that the effects of these variables are key determinants that control whether a bog is a carbon sink or source (Blodau *et al.*, 2004; Lafleur *et al.*, 2005). This is because the carbon balance can be finely poised (Worrall *et al.*, 2006), meaning that differences in temperature or hydrological conditions can alter the sign of the carbon flux from one year to the next (Charman, 2002; Shurpali *et al.*, 1995).

2.3.2 CO_2 fluxes: values from the literature

With the development of the eddy covariance technique and initial studies that pioneered its application in peatland ecosystems (Shurpali *et al.*, 1995), many studies have opted to use this method to measure the NEE of CO_2 at a wide variety of northern peatland sites. However a number of studies have employed various chamber methods, Silvola *et al.* (1996) used manual chambers placed on ground cleared of vegetation at a range of peatlands in Finland. Fluxes from the soils were measured twice weekly and only during the day, but identified significant seasonal variation; springtime fluxes were 18 – 150 mg CO_2 m^{-2} h^{-1} but rose to 600 – 1500 mg CO_2 m^{-2} h^{-1} during warm summer days with low water tables, during the winter months fluxes decreased to 10 – 90 mg CO_2 m^{-2} h^{-1} (Silvola *et al.*, 1996). Most other studies have used larger chambers which include the vegetation component and give estimates of NEE, very few have directly measured soil respiration. In Scotland, Chapman and Thurlow (1996) measured ecosystem respiration by covering large chambers with black plastic drapes to exclude photosynthetic uptake. A deep blanket peat bog released 10 – 20 mg CO_2 m^{-2} h^{-1} during the winter, rising to 60 – 80 mg CO_2 m^{-2} h^{-1} in the summer. A drier area of shallow peat with *Calluna vulgaris* dominated vegetation was also monitored, under these conditions, emissions were significantly higher during the summer months (160 mg CO_2 m^{-2} h^{-1}). At a Canadian ombrotrophic raised bog, Moore *et al.* (2002) reported much higher values of ecosystem respiration (252 – 684 mg CO_2 m^{-2} h^{-1}) during spring/summer and 1296 mg CO_2 m^{-2} h^{-1} during a late-summer dry period. NEE was also measured; during the early period a CO_2 sink of 288 – 792 mg CO_2 m^{-2} h^{-1} was recorded but as respiration increased over the dry period the bog became a source of 36 – 468 mg CO_2 m^{-2} h^{-1}.

An eddy covariance study over two growing seasons revealed substantial variability in CO_2 fluxes at a Minnesota peatland; during a cool, wet summer the site was a sink of about 32 g C m^{-2} as photosynthesis was high and high water-tables limited losses from soil respiration. The following summer was significantly warmer and drier, rates of photosynthesis were depressed while soil respiration was stimulated resulting in a net flux of 71 g C m^{-2} to the atmosphere (Shurpali *et al.*, 1995). Clearly fluxes were highly variable both during a season and between seasons, fluxes ranged from a source of 383 mg CO_2 m^{-2} h^{-1} in the hot, dry summer to a sink of 204 mg CO_2 m^{-2} h^{-1} in the cooler year.

Joiner *et al.* (1999) also reported significant interannual variability, but in this case it was due to different environmental conditions out of the normal growing season. During one summer a Canadian fen was a sink of 91.6 g C m^{-2} but in another year this switched to a source of 30.8 g C m^{-2}. The authors showed that the difference was due to (i) a warm spring and early thaw; and (ii) a warm, dry autumn, both of which stimulated respiration at a time when the vegetation was not photosynthesising (Joiner *et al.*, 1999; Lafleur *et al.*, 1997). A similar growing season study was conducted at a minerotrophic fen in Saskatchewan and found a seasonal sink of 88 g C m^{-2} (Suyker *et al.*, 1997), however it is important to note that measurements were being taken during the peak sink period. At the start (May) the fen was moving from a net source to a sink and again in September the fluxes were reverting to winter-time emissions to the atmosphere, suggesting that an annual budget would be more balanced. Peak mid-summer fluxes were 625 mg CO_2 m^{-2} h^{-1}, relatively high but consistent with the high productivity and water table of the site (Suyker *et al.*, 1997).

Earlier season-long studies had hinted at the seasonal and annual variations in fluxes and the potential importance of winter-time ecosystem respiration in determining annual carbon balances. In the most northerly peatlands, where snow cover is an important feature and can last for long, continuous periods of time, there was a tendency to assume these fluxes were not significant (Sommerfeld *et al.*, 1993). Winter studies, however, have shown that these peatlands are emitting CO_2, which over the whole season can be a significant contribution to the annual carbon budgets, significant enough to change our estimates from sinks to sources (Silvola *et al.*, 1996; Waddington & Roulet, 2000). A number of studies have now been published in which CO_2 fluxes were continuously measured over a whole year (Aurela *et al.*, 2002; Lafleur *et al.*, 2001). Lafleur *et al.* (2001) found a Canadian ombrotrophic bog to be net annual sink of 67 ± 18 g C m^{-2} yr^{-1}, but there was a distinct annual cycle. The mean summer NEE flux was about 116 mg CO_2 m^{-2} h^{-1}, while during the autumn and winter the bog was a fairly constant source of about 45 mg CO_2 m^{-2} h^{-1}. Another annual study identified the same annual cycle in a Finnish subarctic fen but found it to be a smaller net annual sink of approximately 18 g C m^{-2} yr^{-1} (Aurela *et al.*, 2002). In both cases winter-time fluxes to the atmosphere were found to be significant but were more than offset by carbon uptake during the growing season. It is important to note that while these studies reveal important annual cycles, they only show the data for one year and as others have shown, interannual variation can be of great importance. More recently still, the first multi-year measurements have been published. Expanding on earlier studies in Canada, Lafleur *et al.* (2003) showed the carbon budget could change considerably depending on the environmental conditions of that year, a sink of about 70 g C m^{-2} yr^{-1} decreased to near zero in a year with a dry summer.

In the British Isles where winter snow cover and frozen ground are temporary and transient, we might expect winter respiration to be important. Sottocornola and Kiely (2005) found an Irish blanket bog to be a net CO_2 source for four winter months (November to February), but uptake during the summer ensured an overall annual sink of 49 and 61 g C m^{-2} yr^{-1} in 2003 and 2004 respectively. Two years of eddy covariance measurements at Auchencorth Moss, an ombrotrophic raised bog in Scotland, produced an estimate of 28 g C m^{-2} yr^{-1} as the net annual carbon sink (Billett *et al.*, 2004).

Most studies looking at NEE fluxes over any length of time have identified relationships between variations in fluxes and certain environmental factors. In laboratory experiments, CO_2 release increased in a linear relationship as the water-table was lowered (Freeman *et al.*, 1993; Moore & Knowles, 1989). Experimental reduction of water tables by 30 cm was found to increase the net flux to the atmosphere, through a combination of reduced rates of photosynthesis and increased soil respiration (Blodau *et al.*, 2004). In the field EC measurements at numerous sites have shown that decreased

NEE is associated with reduced photosynthesis (Shurpali *et al.*, 1995; Suyker *et al.*, 1997) as well as stimulated respiration (Silvola *et al.*, 1996) at times of high temperature and moisture stress.

Lafleur *et al.* (2005) looked at the environmental controls on ecosystem respiration at a Canadian ombrotrophic bog, which they determined from five years of night-time net CO_2 exchange using EC. Values exhibited an annual cycle, peaking during mid-summer and showed a strong relationship with temperature. Q_{10} values for the peatland were of the order 2.2 – 4.2 which is in the range of other studies (Moore & Dalva, 1993), but Lafleur *et al.* (2005) found near-surface temperature to be a better predictor of ecosystem respiration than temperatures measured at depth. Of particular interest was that ecosystem respiration was not strongly dependent upon water table depth despite considerable fluctuations throughout the period. The authors hypothesised that this was due to the particular peatland being relatively dry causing a complex response in the upper and lower peat profiles and secondly the importance of plant respiration, which was relatively independent of water table (Lafleur *et al.*, 2005). The authors stress the potential strengths of the eddy covariance method for exploring ecosystem respiration when it is combined with high quality data on the environmental variables. Others too have also failed to show the strong relationship between ecosystem respiration and water table level that might be expected and has been shown in other studies. Blodau and Moore (2003) have suggested that there will always be limits to the predictions that can be made from statistical models based on environmental variables, and this may go some way to explaining the lack of correlations in some field studies. They argue that responses to environmental fluctuations are based upon a complex set of interacting production, consumption, storage and transport processes that are unlikely to reach equilibrium over time scales of weeks to months. Because of this, these biogeochemical processes can be said to be decoupled, to some degree, from the observed fluxes to the atmosphere (Blodau & Moore, 2003).

Despite the potential problems associated with modelling peatland carbon fluxes highlighted above, some progress has been made recently (Frolking *et al.*, 2002; Lafleur *et al.*, 2003). Frolking *et al.* (2002) have developed a process-orientated ecosystem model, Peatland CARbon Simulator (PCARS), which simulates carbon flows and storage in a peatland. Photosynthesis, autotrophic respiration, decomposition, methane production and consumption and DOC losses are all calculated. The model is driven by air temperature, PAR, soil temperature, water table depth and drainage data. The model was compared to EC flux measurements of NEE, photosynthesis and ecosystem respiration. Because the model slightly overestimated photosynthesis and ecosystem respiration, these offset one another to produce a NEE value that compared well with the flux measurements. Simulated autotrophic and heterotrophic respiration contributed roughly equally to overall ecosystem respiration (Lafleur *et al.*, 2003).

Eddy covariance yields very useful spatially-averaged values of NEE that are appropriate when determining if a peatland is a carbon sink or source (Aurela *et al.*, 2002; Lafleur *et al.*, 2003; Waddington & Roulet, 2000). However, to explain the magnitude of NEE in terms of the controlling physical, chemical and biological factors, Waddington and Roulet (2000) argue that it is necessary to investigate at a much smaller scale than an EC footprint. This is because these factors and associated fluxes have been shown to vary considerably across small spatial scales in some heterogeneous peatlands. Carbon exchange processes and rates varied significantly with surface topography and location within the peatland, which was due to differences in soil moisture and temperature (Waddington & Roulet, 2000). The authors advocate the use of enclosure methods with a sampling strategy that is stratified according to the whole peatland and surface topography in addition to micrometeorological measurements of NEE.

2.3.3 Methane

As the second most important greenhouse gas in the troposphere, the global methane (CH_4) budget has understandably been the subject of an intensive research effort. The latest estimates place the total methane source at 598 Tg yr^{-1}, which is only partly offset by the annual sink of 576 Tg. The size of the source continues to increase, although there has been a significant reduction in the trend over the last decade. Projections modelled for the next 100 years vary from a continuing trend of increasing concentrations to decreasing atmospheric concentrations depending on source strengths and assumptions about methane reactions with tropospheric hydroxyl radicals (IPCC, 2001).

Natural wetlands are believed to be the largest source of methane (IPCC, 2001); however the world's wetlands are highly variable and flux rates and the processes involved in controlling emissions are similarly variable. Despite covering a relatively small area, tropical wetlands contribute a major part to global methane sources, while northern peatlands are important because of their significant geographic coverage (Gorham, 1991; Kormann *et al.*, 2001). Recently, Kormann *et al.* (2001) described the urgent need for reliable emission measurements from different wetland types in order to improve our understanding of this global source. From a UK perspective there is an increasing emphasis on calculating national emissions and budgets (e.g. The National Greenhouse Gas Inventory), which governments are required to produce as part of their obligations under the Kyoto Protocol (Baggotta *et al.*, 2005). Emissions from peatlands are not included in the UK inventory presumably because current estimates suggest that the contribution is small due to the small geographic area of UK peatland soils (Hargreaves & Fowler, 1998). Nevertheless it is important not to exclude natural methane sources entirely as they are likely to be susceptible to change under future climatic conditions and secondly information about British upland peatlands is likely to be useful when considering other larger areas of northern peatland (Hargreaves & Fowler, 1998; Kormann *et al.*, 2001).

Methane efflux in peatlands is directly dependent on microbial activity and therefore indirectly on soil temperature, water table, vegetation type and the chemical characteristics of the peat (Blodau, 2002). A variety of different anaerobic bacterial groups (methanogens) produce methane in the anaerobic catotelm region of the peat profile (Charman, 2002). Initially organic carbon from decaying plant matter, root exudates or as part of the DOC flow is broken down into smaller molecules by fermentative bacteria. Some of the products of these catabolic reactions such as acetate and hydrogen-carbon dioxide form substrates for the methanogenic bacteria, with methane released as a by-product (Bridgham *et al.*, 1995). Because methane is produced in the catotelm, overall surface flux depends not only on production rates but also on transport to the surface through the acrotelm. Three transport mechanisms are recognised; diffusion, movement as gas bubbles and transport through the aerenchyma of vascular plants (Greenup *et al.*, 2000). In the first two situations methane is highly susceptible to reoxidization to CO_2 by methanotrophic bacteria in the oxidizing environment of the acrotelm (Blodau, 2002). Therefore in certain peatlands, the later method where vegetation acts as a conduit for methane can be important, accounting for 90 % of the total flux (Shannon *et al.*, 1996). It is important to remember that the chemical processes involved are carried out by communities of living organisms which interact with one another and are affected by perhaps small environmental changes. For example, Bridgham *et al.* (1995) point out that methane release, which is part of a global biogeochemical carbon cycle, can be altered by environmental effects on either of the two bacterial groups involved. As obligate anaerobes, methanogens are influenced by the position of the water table; they depend upon being in the water-logged, reducing environment of the catotelm (Blodau, 2002). In situations where the water table is drawn down we expect methane release to decrease as methanogenic activity is restricted to the deeper peat layers and there are greater opportunities for methanotrophs to consume methane prior to release (Blodau, 2002; Charman, 2002). Methane production rates are temperature dependent and to a stronger degree than CO_2 production (average Q_{10} = 4.1 compared to Q_{10} = 2-2.5 for CO_2) (Blodau, 2002). However the methane temperature coefficient is highly variable, for reasons that are not fully understood, but may include methanogens lacking suitable substrates and being poor competitors (Blodau, 2002).

2.3.4 Methane fluxes: values from the literature

In an early effort to quantify the methane flux of Canadian low boreal wetlands, Roulet *et al.* (1992) used chamber methods at 28 sites. Looking at a range of wetland types, the fluxes measured were variable but generally lower compared to other studies (21 mg m^{-2} d^{-1} for bogs). Moisture saturation was found to be the key determinant of high emissions and after this variation could be further explained by peat temperature (Roulet *et al.*, 1992). While the study covered a wide range of different wetland types in an effort to make a region wide estimate of fluxes, these estimates were based on a week long survey at each site during the snow free season and so had limited temporal coverage. Fluxes from fen sites can be considerably higher; Nykänen *et al.* (1995) measured fluxes that were generally 50-200 mg m^{-2} d^{-1} but this increased to 600 mg m^2 d^{-1} during an exceptionally warm summer month.

Micrometeorological methods for measuring methane fluxes were pioneered by Verma *et al.* (1992), they used tunable diode laser spectroscopy in an eddy covariance system to calculate fluxes of 120-270 mg m^{-2} d^{-1} in a Minnesota peatland. The values agreed well with earlier studies using other methods and the temporal variation in fluxes was consistent with changes in temperature and water table level. A similar six day "campaign" style study over a fen in southern Germany found relatively low fluxes of just 5.4 ± 1.8 mg m^{-2} d^{-1}(Kormann *et al.*, 2001). Considering the seemingly favourable conditions (eutrophic and pH neutral peat, high humidity and temperature) the authors found the fluxes to be lower than expected but proposed a number of site-specific reasons. Edwards *et al.* (1994) measured an average flux of 16 mg m^{-2} d^{-1} during a month long study in the summer which compares well to Roulet *et al*. (1992) chamber measurements from similar Canadian bogs.

Annual fluxes have been calculated for a Finnish mire based upon a series of campaign measurements and temperature regression models for the intervening periods (Hargreaves *et al.*, 2001). Average daily fluxes were 15 mg m^{-2} d^{-1}, with peak values being measured during the spring thaw (11 % over 20-30 days). Water table position did not affect emissions as the site was water-logged at all times, while a very strong relationship with peat surface temperature was obtained (Hargreaves *et al.*, 2001). There have been very few studies that have used eddy covariance to measure methane fluxes over longer time periods, Suyker *et al.*'s (1996) season long study identifies the benefits of this approach. They identified diurnal patterns in the fluxes and noted that these patterns varied depending on the time of year. The highest fluxes occurred during mid-summer, fluxes increased from 4.1 mg m^{-2} h^{-1} in early July to a seasonal peak of 19.5 mg m^{-2} h^{-1} on August 1st. A nonlinear regression analysis using water table and peat temperature was able to explain 68-94 % of the variability in methane flux at the site (Suyker *et al.*, 1996).

A search of the literature suggests that only two studies have used eddy covariance to investigate methane fluxes from British peatlands (Beverland *et al*., 1996; Hargreaves & Fowler, 1998). Hargreaves and Fowler (1998) found that over the 14 day period the mean methane emission rate was 15 mg m^{-2} h^{-1}, although there were short periods when the rate was up to four times this value. Methane flux was most strongly influenced by water table depth but there was also a strong linear relationship with peat temperature. Hargreaves and Fowler (1998) used the close relationships between flux, temperature and water table depth together with available meteorological data to produce a simple model to predict fluxes over the whole year. While admitting significant uncertainty and assumptions, this figure was scaled up to yield a value of between 40 and 141 kT as the total annual methane flux from all British wetlands. This would contribute an additional 2-7 % to the current estimate of total UK methane emissions of 2 Mt (Baggotta *et al.*, 2005). Finally the model was used to simulate the effect of possible future changes in temperature and hydrology on methane emissions, a number of realistic scenarios predicted increases up to 35 % (Hargreaves & Fowler, 1998).

Hargreaves and Fowler (1998) found no evidence for systematic variations between night and day fluxes; on the occasions with enhanced daytime fluxes they suggest that the linear temperature relationship is responsible. Other studies have found evidence of a diurnal effect with significantly higher emissions during the day (Edwards *et al.*, 1994), but Suyker *et al*. (1996) found that the difference was only significant at the peak of the growing season (from mid-July) when night-time fluxes were up to 46 % lower. Some have suggested that small changes in conditions such as temperature would be enough to explain small diurnal effects (Edwards *et al.*, 1994), others have argued that different explanatory mechanisms are required (Suyker *et al.*, 1996) It has been suggested that the products of photosynthesis are released into the soils, converted into methane which is then released through the stomata of vascular plants; this photosynthetic effect is then observed as higher daytime emissions (Thomas *et al.*, 1996).

A number of studies have investigated the relationship between methane flux and changes in water table levels experimentally, either in draw-down manipulations (Blodau *et al.*, 2004; Blodau & Moore, 2003; Freeman *et al.*, 1993; Martikainen *et al.*, 1995; Moore *et al.*, 1998) or by comparing natural and drained peatlands (Martikainen *et al.*, 1995; Nykänen *et al.*, 1995). There is a consensus from these studies that lowering the water table of a peatland can significantly reduce fluxes and some evidence for these lower levels to persist upon rewetting (Freeman *et al.*, 1993).

To date there have been many studies quantifying methane fluxes from a range of northern peatlands, these have shown that methane dynamics are highly variable between peatlands. In addition, the few longer-term results suggest a great deal of temporal variability. Clear relationships between environmental variables and flux rates have been identified at certain sites and these have been used to produce simple models to extrapolate results over longer time scales and to make predictions about responses to future climate change.

2.3.5 Fluvial fluxes

A detailed review is beyond the scope of this chapter but for completeness it is useful to consider briefly a number of other means by which carbon can be lost from a catchment, namely the fluvial fluxes. When evaluating the carbon balance of a peatland, it is common for the gaseous exchanges to be measured and then the site is declared a sink or a source. It is relatively rare for studies to measure directly all of the known carbon fluxes and losses due to fluvial fluxes are often overlooked. The fluvial flux can include a number of forms of carbon: dissolved organic carbon (DOC); particulate organic carbon (POC); dissolved inorganic carbon (DIC); and dissolved CO_2. It is true that, in comparison to the major flux pathways of photosynthesis and ecosystem respiration, fluvial exports account for a small part of the carbon budget. However, recent studies that have taken fluvial fluxes into account, have shown that British peatlands that were thought to be significant carbon sinks are close to being carbon neutral or actual sources to the atmosphere (Billett *et al.*, 2004; Worrall *et al.*, 2006; Worrall *et al.*, 2003).

Furthermore, there is increasing evidence that the size of the fluxes, in particular that of DOC, is increasing. Substantial increases in the export of DOC have been observed from UK peatlands and these have corresponded with increased concentrations in streams, rivers and lakes (Evans *et al.*, 2005; Freeman *et al.*, 2001a; Hope *et al.*, 1997; Worrall *et al.*, 2004a; Worrall *et al.*, 2004b; Worrall *et al.*, 2003). A number of reasons have been proposed to explain the observed increases in carbon losses through fluvial fluxes including: rising temperatures (Freeman *et al.*, 2001a); lower water-tables; recovery from acidification; changes in discharge rates; and increasing CO_2 concentrations (Evans *et al.*, 2002; Freeman *et al.*, 2001a; Freeman *et al.*, 2004a; Freeman *et al.*, 2001b; Pastor *et al.*, 2003; Tranvik & Jansson, 2002). Worrall *et al.* (2004a) showed that temperature alone was insufficient to account for the observed DOC increases, while the water table did not change significantly over the time period. Worrall *et al.* (2004a) conclude by favouring an enzymic latch mechanism (Freeman *et* *al.*, 2001b; Freeman *et al.*, 2004b), whereby a period of drought stimulates extracellular soil enzymes causing a step change in DOC production. The fluvial flux is clearly an important pathway in upland ecosystem carbon budgets and one that seems to be susceptible to the effects of climate change, notably warmer temperatures and more periods of summer drought. While it may not be possible to measure DOC as part of every study, it is important not to ignore these fluxes when making judgements about peatland carbon budgets.

2.4 Moor House National Nature Reserve

2.4.1 Location

The studies described in this thesis were carried out at Moor House – Upper Teesdale National Nature Reserve in the northern Pennines of England, in the counties of Cumbria and Durham. The reserve is one of the largest in England and comprises 7387 hectares and a range of upland habitats. The highest point in the Pennines, Cross Fell (893 m), lies to the west of the reserve; to the east of the Pennine ridge are large expanses of blanket bog between 500 – 600 m above sea level, which form the catchment for the sources of the rivers Tees and South Tyne. Measurements and experiments were conducted at Bog End (54° 41’ 27” N, 02° 21’ 50” W; 564 m elevation), amongst this area of extensive blanket bog (Figure 2-1).

2.4.2 Climate

The climate is cool, wet and windy and can be described as “oceanic and subarctic rather than temperate” (Heal & Smith, 1978). A rare long-term upland temperature record exists for the site, measurements began in 1931 and the long-term mean annual temperature is 5.1 °C. An analysis of the record from 1931 to 1995 by Garnett *et al.*, (1997) failed to identify evidence for the significant warming in the 1980s to mid-1990s found elsewhere. Holden & Adamson (2002) reanalysed the record with additional, more recent data and found that the mean annual temperature for 1991 to 2000 had increased to 5.8 °C. Winters are cold, with mean monthly temperatures for December through to February around 1 °C; July and August are the warmest months, with mean temperatures of around 12 °C. The site receives high rainfall and significant snowfall, mean annual precipitation is 2012 mm. In the 1970s, the average snow cover at the Moor House weather station was about 70 days but this has declined to about 50 days in recent years (Holden & Adamson, 2002).

2.4.3 Geology and soils

The surface geology of the site is dominated by horizontal beds of limestone, sandstone and shales from the Carboniferous. A mostly continuous layer of glacial till overlays the solid geology over much of the area of the reserve (Johnson & Dunham, 1963).

Deep peats (around 1 m deep, but up to 7 – 8 m in gullies) are the dominant soil type for more than 50 % of the reserve (Heal & Smith, 1978). In parts of the reserve, deep gullies which cycle between erosion and re-vegetation are important parts of the landscape. At Bog End, the peat is approximately 1.5 m deep and eroding gullies are not common.

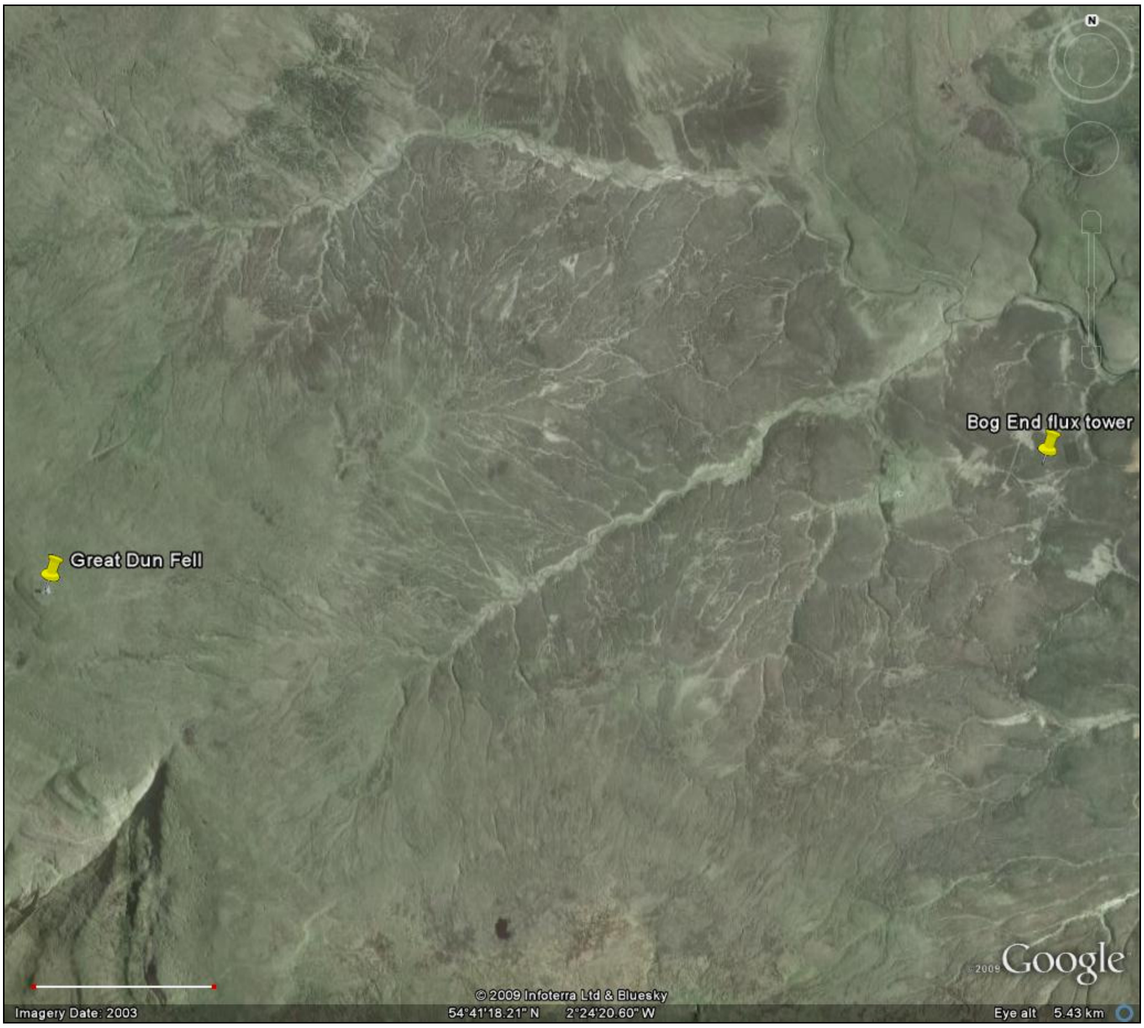


Figure 2-1: A Google Earth image showing part of the Moor House – Upper Teesdale NNR. Great Dun Fell on the Pennine ridge is shown, the large area to the east is predominantly raised bog, with the network of gullies clearly visible in lighter colours. The Trout Beck catchment is at the centre of the image, with the River Tees itself to the north. The scale line at the bottom left represents one km.

2.4.4 Vegetation

The vegetation at Moor House was extensively described by Eddy et al. (1968) and the plant communities at Bog End can be seen as typical of those growing on the acid, waterlogged peats which cover half of the reserve. Lying above the present-day tree line (Heal & Smith, 1978), the vegetation has been classified as Calluneto-Eriophoretum, (Eddy *et al.*, 1968) and is dominated by *Calluna vulgaris*, *Eriophorum vaginatum* and *Sphagnum* spp. (Figure 2-2). The vegetation appears as an even patchwork of *Calluna* bushes interspersed with tufts of *Eriophorum,* moss species existing mostly as an under storey although occasionally in small open patches. Minor species present include, *Empetrum nigrum*, *Rubus chamaemorus* and *Eriophorum angustifolium*. There are two other plant communities which account for relatively small areas of the Bog End study site. There are small areas where the water table is generally higher and close to water courses, where the *Sphagnum* spp. are more dominant and patches of *Juncus effusus* can be found, classified as Sphagneto-Juncetum effusi (Eddy *et al.*, 1968). Additionally, a narrow strip identified as Juncetum squarrosus sub-alpinum (Eddy *et al.*, 1968) is found at the base of a slight rise in the topography. In addition to *Juncus squarrosus*, tufts of *Festuca ovina* and *Deschampsia flexuosa* are found and mosses are represented by *Sphagnum* spp and *Polytrichum commune*.

Figure 2-2: A photograph taken at Bog End looking east. The typical Calluneto-Eriophoretum vegetation is visible in the foreground, with the raised plateau of peatland extending towards the Pennine ridge of Great Dun Fell, Little Dun Fell and Cross Fell.

2.4.5 Management

Since being designated as a National Nature Reserve in the 1950s, the area has been the subject of relatively low levels of management. Previous to this, the site was operated as a commercial grouse moor, heather burning and ‘gripping’ (digging drainage ditches) being carried out on parts of the reserve. Today, grips are not maintained, heather burning only occurs on small plots, as part of a long-term experiment, and shooting is not permitted. Very low levels of sheep grazing are maintained on parts of the reserve (including Bog End) from late spring to autumn.

2.5 A brief history of relevant research at Moor House

2.5.1 Establishing a long-term climate record

As a site of research into upland ecology, Moor House has a rich and enviable history of past studies. With well over a hundred published papers with relevance to ecosystem carbon cycling and processes, the amount of baseline information, knowledge and ancillary data forms an extremely useful resource to current researchers.

In the early 1930s Gordon Manley established a meteorological station at the site publishing several papers (Manley, 1936) on the climate of the north Pennines and setting the precedent for observations that now constitute a long-term and close to continuous record (Garnett *et al.*, 1997; Holden & Adamson, 2002; Manley, 1936). During this early period the surrounding land was in private ownership and managed as a grouse moor, while a network of rough tracks, remnants of the past mining activities, allowed access to this otherwise remote and marginal landscape. In 1952 the area was acquired by the Nature Conservancy and designated a National Nature Reserve, with the aim not only of conservation but also to establish it as a site for scientific research.

2.5.2 1950s - Land use and management

In the early years, in addition to studies describing the nature of the area and its basic ecology (Gorham, 1953, , 1956; Pigott, 1956), there was an emphasis on understanding the limits of plant growth in this marginal environment (DeSutter *et al.*, 2008; Gore, 1961a, 1961b, , 1963) and experiments were established to determine the requirements for establishing commercial forestry plantations on the blanket bog (Nature Conservancy, 1952-1980).

2.5.3 1960s and 1970s – IBP and production ecology studies

During the period of The International Biosphere Programme, there was a shift from more applied work to a study of the basic production ecology of the blanket bog system. Productivity was studied in terms of material accumulated over an annual time scale and determined by field cropping. Detailed studies produced production estimates by species and by plant community and these were conducted at a range of blanket bog sites across the reserve, so that the effects of altitude, water table and management could be examined (Smith & Forrest, 1978). Clymo and Reddaway (1974) concentrated on estimating production values for *Sphagnum*, while others measured the main vascular species composing the *Calluneto-Eriophoretum* blanket bog (Forrest, 1971; Forrest & Smith, 1975). A threefold variation in total net production of the blanket bog was found, from 300 to 900 g DM m^{-2} yr^{-1}, including low values from wetter *Sphagnum* dominated sites and higher values from recently burnt sites; the mean value across seven sites was 659 ± 53 g DM m^{-2} yr^{-1} (Smith & Forrest, 1978).

A second aspect of the IBP work of relevance to this study was studies on the rates of decomposition of organic matter. Following a similar approach to the production studies, decomposition in terms of loss of material over time (g g^{-1} yr^{-1}) was determined for plant components (e.g. shoots, stems, leaves, etc.) using litter bag experiments (Clymo, 1965; Heal *et al.*, 1978; Latter & Cragg, 1967).

2.5.4 Recent research – A focus on carbon

There was revival in long-term monitoring at Moor House when, in 1992, it was designated a terrestrial and freshwater (Trout Beck) site as part of the newly established Environmental Change Network (ECN). An automatic weather station is maintained, which is complemented by continuous measurements of water table depth and stream discharge. Precipitation, soil and stream water are collected weekly and analysed for chemical content. On a less regular basis, records are made of land use, vegetation and soil carbon content (Sykes & Lane, 1996).

Linked to earlier work, and often making use of continuous long-term climate data made available by the ECN monitoring programme, a number of recent publications detail work looking at the peatland in the context of environmental change. Worrall and others have looked extensively at the dissolved organic carbon fluxes from streams at Moor House (Worrall *et al.*, 2005, , 2006; Worrall *et al.*, 2008), while Evans and Warburton (2005) quantified the carbon losses as fluvial particulates and sediments. A number of publications have built on these data to produce 'complete' carbon budgets for catchments within the Moor House reserve (Worrall *et al.*, 2007b; Worrall *et al.*, 2003). However, the gaseous carbon fluxes (GPP, soil respiration and methane flux) were largely based on empirical relationships and were not calibrated with measurements made within the catchment. Details of these carbon budget studies were described in section 2.2 of this chapter.

The long-term grazing and burning experiments established in the 1950s and maintained in the interim have been revisited in order to look for effects of land use on gaseous and dissolved carbon fluxes (Clay *et al.*, ; Garnett *et al.*, 2000; Ward *et al.*, 2007; Worrall & Adamson, 2008; Worrall *et al.*, 2007a). Looking at peat carbon content, Garnett *et al.* (2000) found that whereas low intensity sheep grazing did not affect carbon accumulation, burning on a decadal cycle significantly reduced carbon sequestration by an estimated 73 g m^{-2} yr^{-1}. Ward *et al.* (2007) found carbon accumulation was reduced by 25 g m^{-2} yr^{-1} after burning at the same site and also identified a less significant grazing effect. Using gas flux measurements, they found higher rates of carbon turnover (increased photosynthesis and respiration) on burned and grazed plots, which they attributed to changes in plant community structure.

2.6 Conclusions

There are a variety of proven techniques for making long-term continuous measurements of gaseous carbon fluxes such as eddy covariance for ‘landscape averaged’ fluxes and chamber techniques for partitioning flux pathways or evaluating spatial variation. A good deal is known about carbon cycling in peatlands and the processes involved, but gaps in our knowledge exist due to the apparent considerable differences in fluxes and their control mechanisms between and within peatlands. Moor House – Upper Teesdale NNR has been a site of relevant research for more than 60 years. There are clear advantages to working there, a great deal is known about the ecosystems and further work to address the gaps in the knowledge for the site will contribute to a more complete understanding of the area itself and the uplands of the British Isles as a whole.

CHAPTER 3

NET CO_2 FLUXES AT THE LANDSCAPE SCALE

3.1 Introduction

3.1.1 Scope

The net CO_2 flux or net ecosystem exchange (NEE) incorporates a number of individual carbon fluxes which are often the pathways by which most carbon is cycled within an ecosystem. It is the sum of important processes including photosynthesis, plant and soil respiration. Whilst the component fluxes are almost always large, the size and sign of the net flux can be highly variable depending on the relative size of the components. A highly positive NEE can result in an ecosystem where CO_2 uptake by photosynthesis is significantly outweighing respiratory losses, such as a growing forest or agricultural crop or alternatively in a peatland where the respiration term is suppressed. Alternatively an ecosystem may be a net source of CO_2, for example a peatland in which peat accumulation has ceased and more CO_2 is respired than is fixed through photosynthesis.

3.1.2 Aims

This chapter aims to quantify the net CO_2 flux over an area of blanket bog at Moor House NNR. The following research questions are addressed:

- Is the blanket bog at Moor House a net sink or source of CO_2 over an annual time scale?
- Can the measured net flux be successfully partitioned into its component fluxes?
- How much CO_2 is fixed by photosynthesis and how much is respired back to the atmosphere by the plants and soil microbes?
- What are the important environmental factors driving the variation in net CO_2 fluxes?
- How important are winter-time fluxes in determining the annual CO_2 flux?
- Is there any evidence of interannual variability in the net CO_2 flux?

3.2 Methods

3.2.1 Field site

An eddy covariance system was established at the Bog End area of the Moor House reserve (54° 41’ 27” N, 02° 21’ 50” W; 564 m elevation) on 06 July 2006. The reserve and field site are described in detail in section 2.4. With the exception of one clearly defined sector, the fetch was uniformly blanket bog, with the majority being made up of the Calluneto-Eriophoretum plant community, dominated by *Calluna vulgaris*, *Eriophorum vaginatum* and *Sphagnum* spp. (Eddy *et al.*, 1968). The exception was a small (0.8 ha) experimental conifer plantation which lay 150 m to the north east (between 40 and 90 degrees). Only a small proportion (2.5 %) of half-hour fluxes originated from this sector and these were excluded from further analysis. Over a scale of 300 m in all directions from the flux tower, the terrain was gently sloping from south-west to north-east. Peat depth within the flux footprint was between 1 and 1.5 m.

3.2.2 Field instrumentation

The eddy covariance system consisted of a CSAT3 sonic anemometer (Campbell Scientific Inc, Logan, Utah, USA) to measure the vector components of the wind and a LI-7500 open-path IRGA (Li-Cor Inc., Lincoln, NE, USA) to measure the atmospheric concentrations of CO_2 and H_2O. Ancillary measurements of environmental variables were made using the following instruments: air temperature and relative humidity by a HMP45C (Campbell Scientific Inc.); net radiation by a NR-Lite net radiometer (Kipp and Zonen, Delft, The Netherlands). Soil sensors were installed in four soil pits 3.5 m from the base of the flux tower. The volumetric water content of the peat was measured using two CS616 water content reflectometers (Campbell Scientific Inc.) installed at a depth of 8 cm below the peat surface. Soil temperature was determined at a depth of 7 cm to 10 cm by four TCAV-L averaging soil thermocouple probes (Campbell Scientific Inc.). Measurements of soil heat flux were provided by four HFP01 soil heat flux plates (Hukseflux Thermal Sensors, Delft, The Netherlands).

Raw data outputs from the sonic anemometer and IRGA were logged continuously at a frequency of 10 Hz by a CR5000 datalogger (Campbell Scientific Inc.). The datalogger also ran a program which generates on-line half-hourly fluxes and stores these alongside half-hourly measurements of the environmental variables. Additional sensors were monitored by two DL2e dataloggers (Delta-T Devices Ltd, Cambridge, UK). These comprised: a QS2 quantum sensor measuring photosynthetically active radiation (PAR); soil temperature sensors within the canopy, and at 2.5 cm, 7.5 cm and 15 cm below the surface (three sensors at each depth). A custom built-sensor (Electronics Workshop, Biology Department, University of York, UK) measured the depth from the peat surface to the water table in a dipwell 4 m from the flux tower.

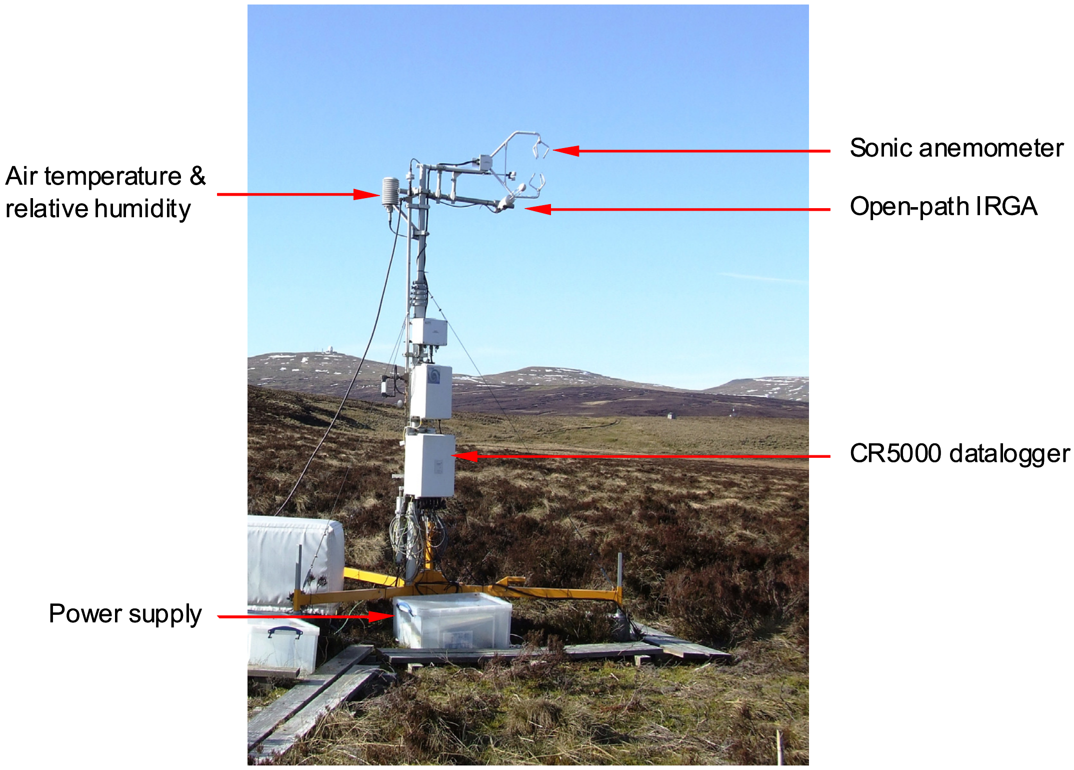


Figure 3-1: A photograph showing the Bog End flux tower and associated instruments. Net radiation and PAR sensors were mounted on a separate mast nearby and soil sensors were placed in pits four metres from the base of the tower.

Initially the flux tower and associated instrumentation were powered by a 12 V battery charged by an array of six solar panels positioned at the base of the tower. The system was modified in February 2007 to take account of the significant power requirements of the TGA100a methane analyser. An array of 12 solar panels, a wind turbine and a back-up propane generator charged a large battery bank located 100 m south of the flux tower. This system supplied 240 V power to the flux tower (required by the TGA100A) which was also used to maintain charge in the 12 V battery at the base of the tower. Under normal circumstances, when only CO_2 fluxes were being measured, the output from the solar panels and wind turbine was more than sufficient, with the propane generator only being used during methane campaigns. The gas generator was set to start automatically when required and the output logged, to allow any exhaust effects on the measured fluxes to be monitored.

3.2.3 Gap-filling environmental data

Precipitation and solar radiation were not measured at Bog End, but these data were available from the Moor House Environmental Change Network (ECN) automatic weather station (54° 41’ 24” N, 02° 22’ 34” W, 550 m elevation) which is 750 m west of the flux tower. ECN data were also used to fill gaps in the Bog End record of air temperature, soil temperature, relative humidity and net radiation that arose as a result of instrument or power failure. Correlation between the two air temperature records showed a good fit and ECN data were inserted into the gaps in the Bog End record using the regression equation:

$$\mathrm{BogEndtemp} = 0.9427\ \mathrm{ECNtemp} - 0.2117 \quad R^2 = 0.97 \qquad \textbf{(3.1)}$$

The quantum sensor for PAR measurements was installed two months after the EC system, for this period, PAR was calculated from solar radiation data using a relationship developed for the same period in the following year (Britton and Dodd, 1976):

$$\mathrm{PAR} = 1.9103\ \mathrm{SR} + 6.1817 \quad R^2 = 0.96 \qquad \textbf{(3.2)}$$

3.2.4 Processing eddy covariance data

Raw data were post-processed using EdiRe, a software package developed by John Moncrieff and Robert Clement at the University of Edinburgh (www.geos.ed.ac.uk/abs/research/micromet/EdiRe/). EdiRe is a flexible tool which allows the user to build up a processing list based on their requirements and those of their particular field site. The complete processing list used to calculate fluxes at Bog End is included in Appendix 1, but a description of the routine follows below.

Half-hour fluxes of CO_2, latent heat and sensible heat were calculated as the covariance of the deviations from the mean of the vertical wind velocity and scalar concentrations following the methodology set out by Aubinet *et al.* (2000). The high-frequency raw data streams were first subject to a despiking routine similar to Hojstrup (1993), based on standard deviation from the half-hour mean. A planar fit coordinate rotation was applied to the three velocity components (Wilczak *et al.*, 2001), and sonic anemometer air temperature was corrected for humidity fluctuations (Schotanus *et al.*, 1983). Frequency response corrections to account for sensor path lengths and sensor separation were applied to all fluxes (Moore, 1986). Finally, density fluctuation corrections, so called Web-Pearman-Leuning corrections (WPL), were applied to CO_2 and latent heat fluxes (Webb *et al.*, 1980).

The storage term of CO_2 between the vegetation and the measurement height was ignored. The term is routinely calculated for forest systems where tall vegetation and measurement heights of tens of meters mean that storage could be significant. An accurate estimate requires profile measurements of CO_2 concentrations at a number of heights above the land surface. However, at low measurement heights over short vegetation, the term is expected to be insignificant (Baldocchi, 2003) and has been justifiably ignored in similar studies to that reported here (Rogiers *et al.*, 2008).

The sign convention is such that with the exception of radiative fluxes, positive values indicate a flux away from the surface and negative values show a flux towards the surface.

3.2.5 Data quality control

As discussed earlier, spikes in the raw ten Hz data streams were addressed automatically within the EdiRe processing routine. Visual checks of the half-hour means showed that values of sensible heat, latent heat and CO_2 fluxes required further quality control. The majority of these unreliable half-hour fluxes were associated with precipitation events, under which conditions the open-path LI-7500 IRGA is prone to yield erroneous CO_2 and H_2O concentrations (LI-COR, 2004). Such half-hours were flagged based on the IRGA's 'AGC' output which is sensitive to the presence of precipitation within the open-path. This procedure eliminated the majority of the unusual fluxes (unexpectedly high or low fluxes or fluxes of an unexpected sign for the time of day). Some spikes remained and examination suggested that a second flag was necessary, based on highlighting fluxes when the standard deviation of the mean half-hour CO_2 concentration was high. In some eddy covariance studies, an important quality control issue is the problem of low turbulence, stable conditions on calm nights. It is possible that at some sites, CO_2 exchange is underestimated during such conditions when the assumptions of the eddy covariance method may not be met (Goulden *et al.*, 1996, Aubinet *et al.*, 2000). Night-time fluxes were examined with reference to the friction velocity (as a measure of the degree of turbulent mixing), to determine if there was evidence of this problem and if further filtering of night-time data was necessary.

3.2.6 Gap filling

Short gaps of less than two hours were filled by linear interpolation, longer gaps in the time series of CO_2 fluxes were filled using the output from a Photosynthetic Irradiance Response and Temperature sensitive respiration (PIRT) model, in which relationships of CO_2 fluxes to environmental variables were developed (Williams *et al.*, 2006). Good quality night-time data ($SR < 0$) were plotted against soil temperature and a modified Arrhénius equation (Lloyd and Taylor, 1994) was fitted to the data (Aubinet *et al.*, 2000). The parameters R_b and β were fitted to the data set using the Solver function in Microsoft Excel to reduce the Root Mean Square Error (RMSE) and this parameterised model was used to fill night-time gaps in the flux record.

Day-time fluxes were viewed as ER minus GPP and in order to fill day-time NEE gaps, both components were estimated for each half-hour. Firstly, the parameterised respiration model was run and these estimates of day-time ER were added to the measured NEE values to give estimates of GPP. GPP was then plotted against PAR and a hyperbolic curve fitted in order to generate parameters for the Photosynthetic Irradiance Response model. Photosynthetic parameters were estimated separately for the seasonal periods (June-Aug, Sept-Nov, Dec-Feb and Mar-May); the full PIRT model was used to fill day-time gaps:

$$\mathrm{NEE} = R_b\, e^{\beta T} - \frac{P_{\max} I}{k + I} \tag{3.3}$$

where, R_b is basal ecosystem respiration at 0°C (μmol CO_2 m^{-2} s^{-1}), β is the relative increase in respiration with soil temperature, T (°C). $P_{\max}$ is the rate of light saturated photosynthesis (μmol CO_2 m^{-2} s^{-1}), k is the half-saturation constant of photosynthesis (μmol PAR m^{-2} s^{-1}) and I is the photosynthetic photon flux density (μmol m^{-2} s^{-1}).

3.2.7 Flux partitioning

Net CO_2 fluxes were partitioned into GPP and ER; for half-hours for which NEE measurements were not available, estimates of the partitioned fluxes were generated as part of the gap-filling procedure described above. For half-hours for which NEE was measured, during the night-time, ER was equal to NEE. During the day, ER was estimated from the temperature response model, and GPP was then calculated as equal to measured NEE minus modelled ER.

3.2.8 Uncertainty analysis

Random errors include those originating from statistical uncertainties of the EC method as well as those associated with factors such as the varying flux footprint. Further uncertainty resulting from NEE gap-filling may also contribute to the total random error (Aurela *et al.*, 2002). A methodology has been developed, whereby the random error is calculated from the difference between observed (NEE_{obs}) and modelled (NEE_{mod}) 30 minute NEE fluxes:

$$E_r = \sqrt{\sum_{i=1}^{n} \frac{\left(\text{NEE}_{\text{obs}} - \text{NEE}_{\text{mod}}\right)^2}{(n-1)\,n}} \tag{3.4}$$

where, n is equal to the number of 30 minute periods for which both NEE_{obs} and NEE_{mod} are available.

Some studies have used the 'error' calculated from the energy balance closure as a correction factor, often resulting in an increase in the magnitude of the fluxes. However, there are also significant uncertainties associated with energy balance estimation itself. Therefore, rather than use the calculated offset as a correction factor, the approach of Sottocornola and Kiely (2005) was used, whereby it provided an estimate of the systematic error of the system. An estimate of the total uncertainty (E) was obtained by calculating the root of the sum squares of random (E_r) and systematic errors (E_{sys}):

$$E = \sqrt{{E_r}^2 + {E_{sys}}^2} \tag{3.5}$$

3.2.9 Data analysis

Curve fitting and parameter estimation were performed with a combination of the Solver function in Microsoft Excel and Regression Wizard in SigmaPlot 10 (Systat Software, Inc.). One way analysis of variance (ANOVA) with a Tukey's *post-hoc* test was used to establish whether night-time fluxes from periods with low friction velocities were significantly lower than fluxes measured when friction velocities were higher (SPSS version 12.0.1, SPSS Inc, Chicago, Illinois, USA).

3.3 Results

3.3.1 Environmental conditions

In this study, data on the net fluxes of CO_2 were collected for a period of 21 months from July 2006 through to the beginning of April 2008. Figure 3-2 shows how monthly air temperature and precipitation recorded during the study period compared to the long-term monthly averages from the Moor House ECN weather station. Apart from August, summer months in 2006 were warmer than average, with July also being markedly drier. The winter of 2006/07 showed close to average monthly temperatures, with December and January being wetter than normal. April 2007 was both considerably warmer (+2.55 ºC) and drier (-101 mm) than the 16 year averages. While July was cooler (-1.80 ºC), the remainder of the growing season experienced close to average monthly temperatures. Higher than average precipitation occurred in June and July. The mean annual air temperature at Moor House is 6.10 ºC; the values for 2006 and 2007 were close to this long-term average at 6.19 and 6.06 ºC respectively. In terms of total annual precipitation, both years showed similar values to the long-term average of 2012 mm, with 2007 being slightly wetter (2062 mm) than 2006 (1921 mm).

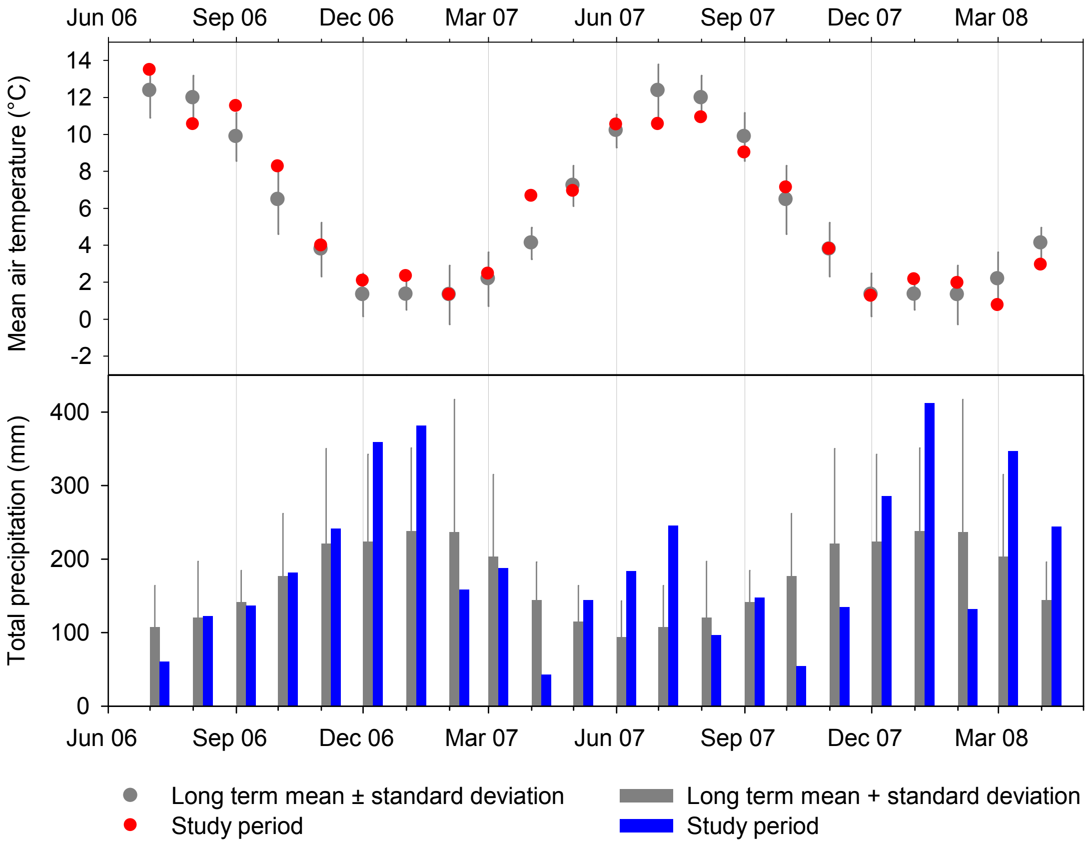


Figure 3-2: Monthly climate variables for the study period (July 2006 to April 2008) in the context of long-term monthly means ± one standard deviation (1992 to 2008). Based on data from the Moor House ECN automatic weather station.

Meteorological data collected at the Bog End flux tower site, and used for flux gap-filling exercises and later analyses, are presented in Figures 3-3 and 3-4. The summer of 2006 saw a number of relatively hot days, with daily means approaching 20 ºC on a number of occasions and a peak temperature of 26.25 on 18th July; such conditions were not seen during the cooler summer of 2007. Mean daily temperatures can drop below zero from October through to March, although such occurrences are not prolonged, with fluctuations being common. A low of -9.25 ºC was recorded during the morning of 21st December 2006.

Significant precipitation events can occur during any month of the year, although the majority fall during the winter months. The peat was found to be close to water-saturated (see soil moisture, VWC) for most of the time between October and

March. During the summer both soil moisture and depth to the water table are seen to respond rapidly to periods of precipitation and dryness. During the measurement period, the water table was rarely recorded at the peat surface; the mean was 8 cm below the surface; after a dry spell, this could drop to 20 cm below the surface.

For the vast majority of the time, winds originated from a sector from the south-west to the north-west, with the average vector being 254 degrees.

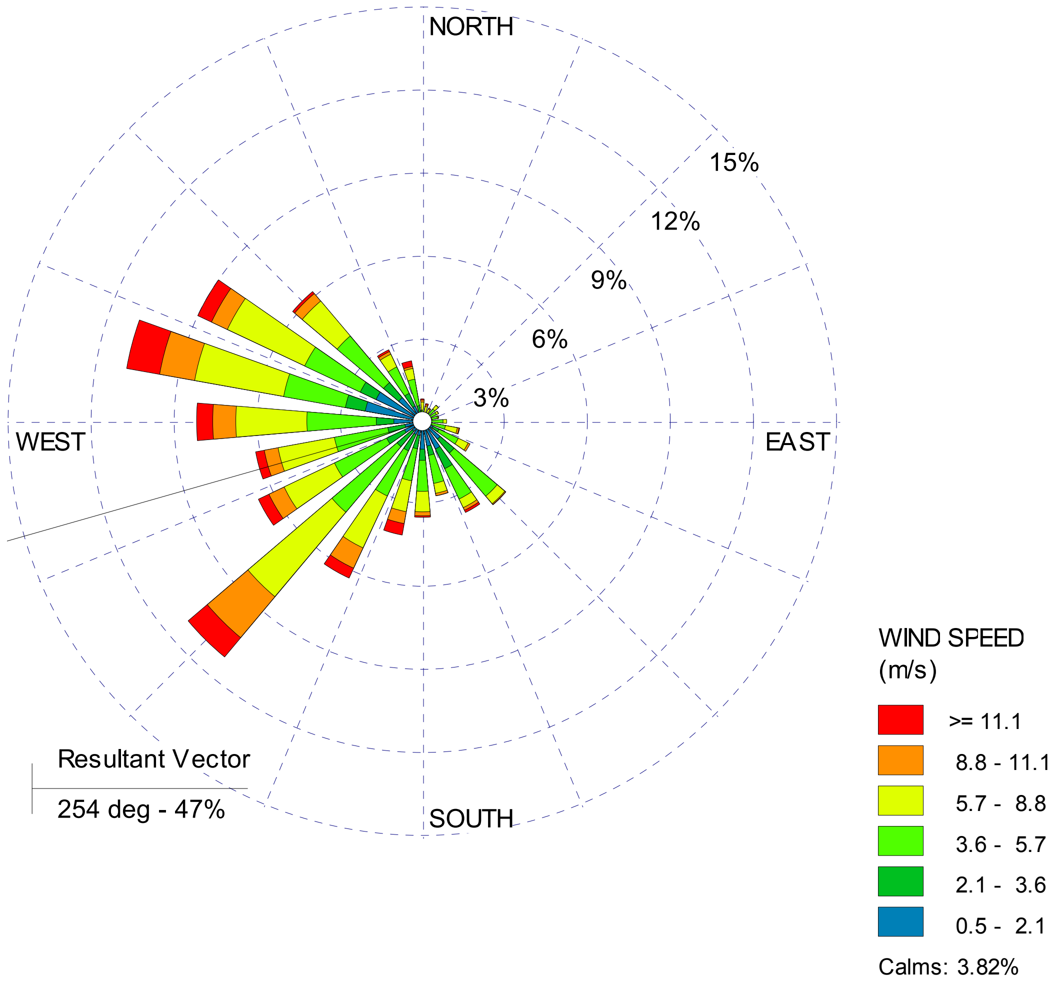


Figure 3-3: Wind rose plot of wind speed (m s^{-1}) and wind direction (degrees) at the Bog End flux tower for the period 06 July 2006 to 03 April 2008. Wind directions are divided into 15 degree bins, the length of spokes relates to the frequency of time that the wind blows from a particular direction and the colours depict the frequency that the wind blows at a range of speeds.

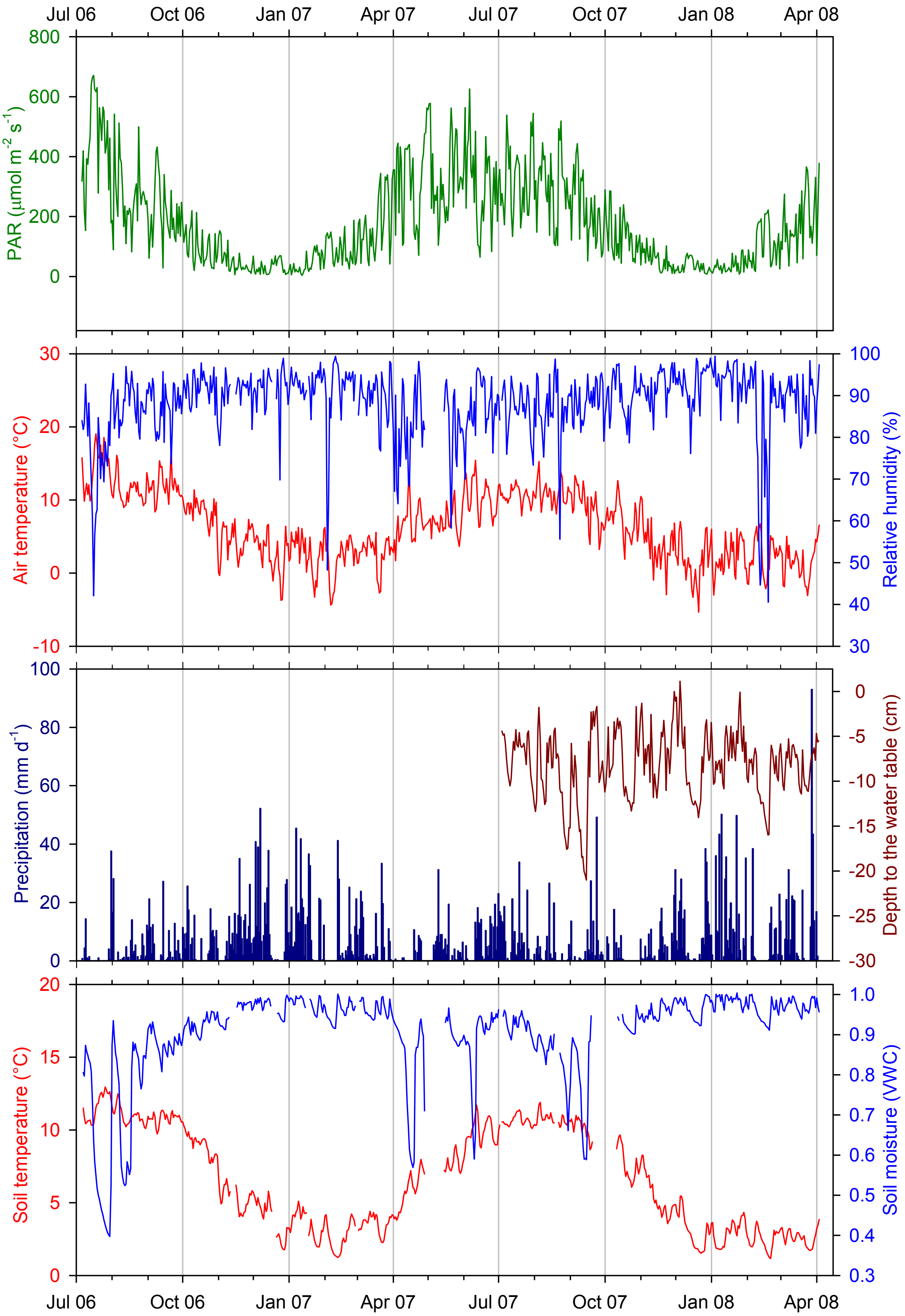


Figure 3-4: Mean daily climate variables measured at the Bog End flux tower for the period 06 July 2006 to 03 April 2008.

3.3.2 Data capture

For CO_2 fluxes, 40 % of half-hours during the measurement period were classified as having good quality data. While, this figure represents a relatively high proportion of 'missing' data, a relatively low number were as a result of instrument or power failure (9 %) the majority were due to quality control of data based upon precipitation effects on the sensors. Attempts were made to reduce these effects, such as applying Rain-X rain repellent to the lenses of the open-path IRGA and adding 'wicks' to the transducer heads of the sonic anemometer, as recommended by the manufacturers. It is an unfortunate fact that an open-path sensor will inevitably suffer significant data loss in a wet climate such as the northern Pennines. Progress with addressing this acknowledged problem has been reported in a recent publication: Clement *et al.* (2009) modified an open-path IRGA to enclose the sensor head and added a short intake tube and small pump. They achieved increased good quality data capture by 10-25 % compared to an unmodified open-path IRGA at two test sites. Developments such as these will make open-path sensors a more attractive proposition in wet climates where power limitations prevent the use of traditional closed-path sensors.

3.3.3 Energy balance

The surface energy balance of the bog surface can be described by equation 3.6:

$$R_n - G - H - LE = 0 \tag{3.6}$$

where, R_n is net radiation, G is the soil heat flux, H is the sensible heat flux and LE is the latent heat flux (all units are W m^{-2}). The energy available to the system in terms of net radiation and the heat flux into or away from the soil should be balanced by energy expended by processes contributing to the latent and sensible heat fluxes. Figure 3-5 shows the energy budget for the Bog End site for the duration of the study; net radiation and soil heat flux were measured close to the flux tower, while the turbulent fluxes were calculated using the eddy covariance method.

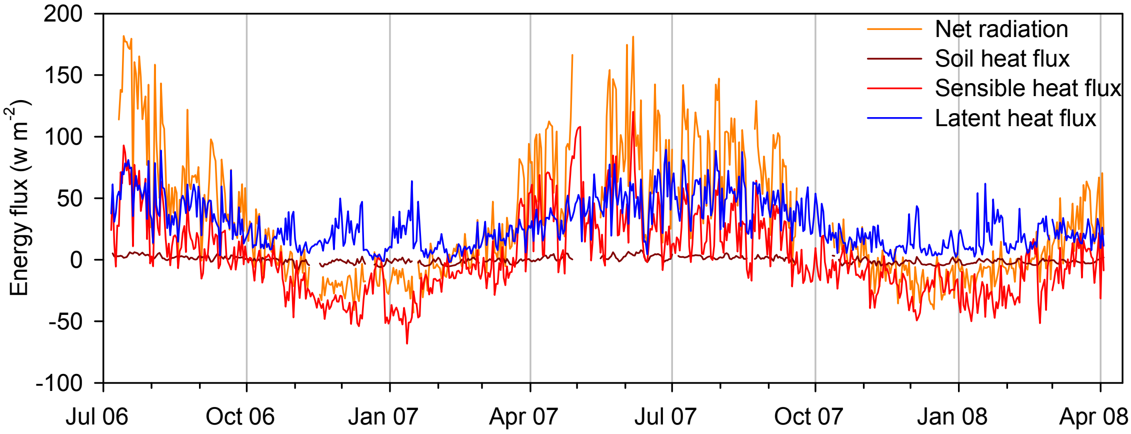


Figure 3-5: Measured and calculated components of the energy budget for the Bog End flux tower. Data are daily means, sensible and latent heat fluxes include gap filled data to account for missing portions of the day due to data quality control. The sign convention is such that with the exception of net radiation, positive values indicate energy transfer away from the surface and negative values show transfer towards the surface.

The ability to balance these terms and 'close the energy budget' can be seen as an indication as to how well or poorly the turbulent fluxes have been captured by the eddy covariance system. The results of an investigation into the energy balance closure are presented in Figure 3-6, where available energy for a half-hour ($R_n - G$) is plotted against the sum of the latent and sensible heat fluxes ($H + LE$) for the same period, calculated by the eddy covariance method. A 1:1 relationship would indicate complete closure of the energy budget, the regression lines and equations show the actual relationship under a number of scenarios. The results of an initial processing run (Figure 3-6a), with no corrections applied to *LE* or *H* show that energy closure was relatively poor at just 73 %, suggesting that 27 % of the measured available energy was not unaccounted for or 'lost' from the flux calculations. Applying frequency response corrections to *LE* and *H* to account for the inability of the system to measure very high and low frequency signal fluctuations improves the estimate of energy budget closure to 79 % (Figure 3-6b). Figure 3-6c shows the effect of both frequency response corrections and the application of Webb-Pearman-Leuning (WPL) density corrections to the *LE* flux, an energy budget closure of 82 % is estimated after this final processing of the fluxes.

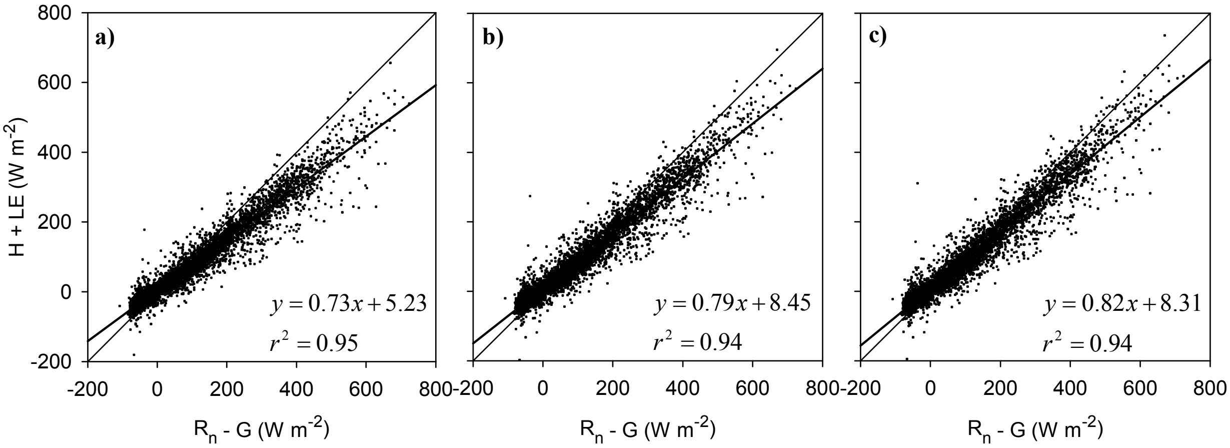


Figure 3-6: Estimation of the energy balance closure. Data are half-hour averages of the available energy, net radiation (*R_n*) minus soil heat flux (*G*) plotted against the sum of sensible (*H*) and latent (*LE*) heat fluxes measured by eddy covariance. Linear regression lines (thick solid line) and equations are shown. Plots show the effect of employing corrections while processing eddy covariance data: a) despiking only, b) despiking plus frequency response corrections applied to *H* and *LE*, c) despiking, frequency response and WPL corrections applied to *LE*.

Night time CO_2 flux data were examined for potential friction velocity effects on the observed fluxes. In monthly plots of night time CO_2 flux against friction velocity, there was no discernable threshold, below which the magnitude of the flux dropped off (Figure 3-7a). Additionally, half-hour fluxes were binned into nine friction velocity categories and their means compared. There was no evidence of significantly lower fluxes or greater variation under low friction velocities which has been reported by some but not all eddy covariance studies (Figure 3-7b); therefore, a friction velocity filter was not applied to the dataset. The time series of quality controlled half-hour net CO_2 fluxes for the measurement period is presented in Figure 3-8.

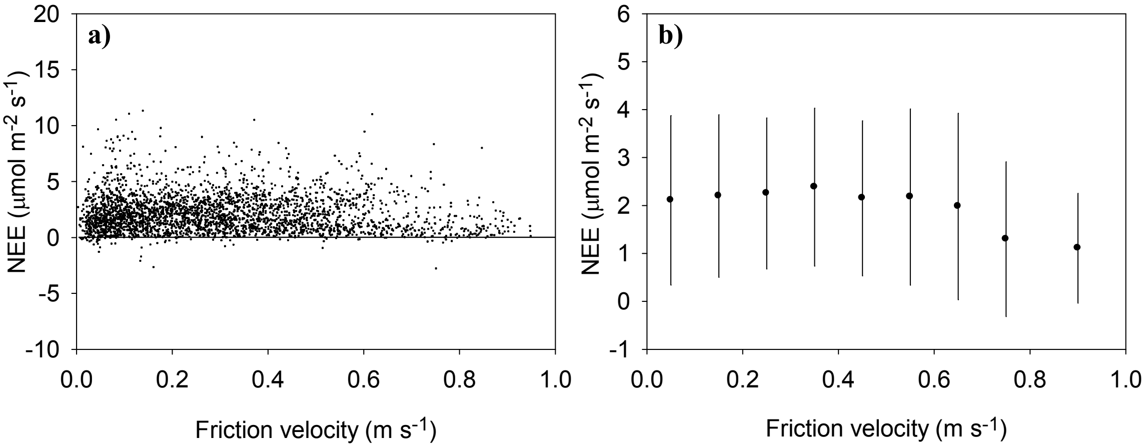


Figure 3-7: Relationship between night time net ecosystem exchange (µmol m^{-2} s^{-1}) and friction velocity (m s^{-1}) for the study period. a) Points are half-hour average values; b) NEE vales were binned into nine friction velocity categories, points are mean values ± standard deviations. NEE was not significantly lower at low *U values; $p < 0.05$.**

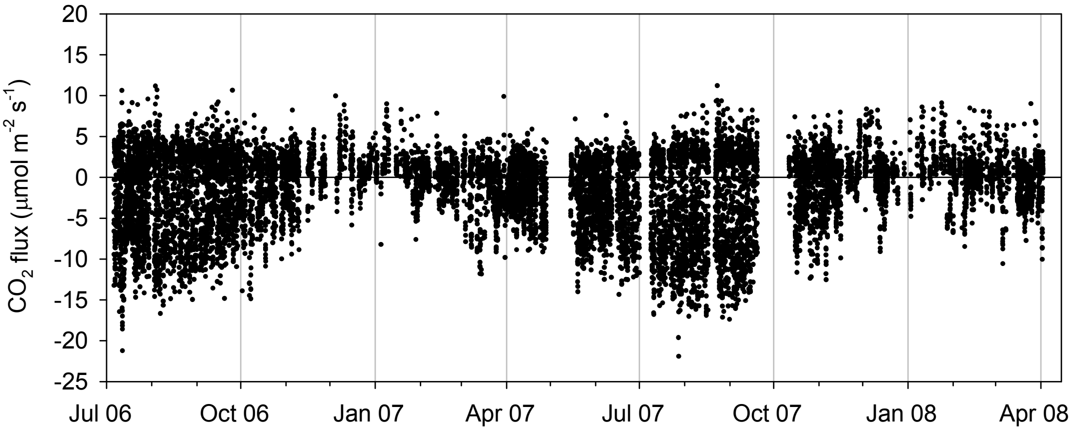


Figure 3-8: Half-hour CO$_2$ fluxes (µmol m^{-2} s^{-1}) calculated from measurements made at the Bog End flux tower. Negative values indicate net uptake; positive values represent net emission.

3.3.4 Temperature effects

Soil temperature explained a greater proportion of the variation in night-time CO_2 fluxes than air temperature. There is a good deal of scatter in the relationship when half-hourly flux data are used (Figure 3-9) although this is reduced when average night-time values (data for six or more half-hours available) for NEE and temperature are used (R^2 of 0.49 for air temperature and 0.67 for soil temperature; data not shown). However, the relationships presented in Figure 3-9 were deemed most appropriate for gap-filling the half-hour NEE time series. The Q_{10} coefficient of ecosystem respiration was estimated to be 2.16 based on air temperature and 3.86 based on the soil temperature relationship.

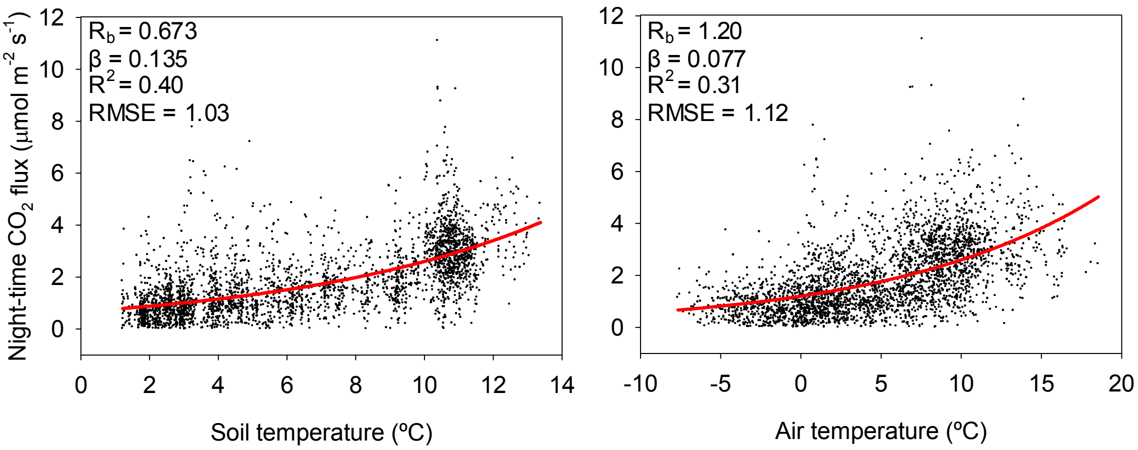


Figure 3-9: Relationship between night-time CO_2 flux (assumed to be ER) and temperature. Symbols are half-hour eddy covariance measurements; red lines show predictions of the temperature response model fitted to the data.

3.3.5 Water table and soil moisture effects

There was no evidence of an effect of water table depth on measured night-time ecosystem respiration fluxes. For the periods for which data were available, the water table varied between a high of 2.6 cm and a low of 21 cm below the peat surface. There was no significant relationship between night-time ER and depth to the water table; neither could water table explain any of the variation in the residuals of the regression of observed ER against soil temperature modelled ER (Figure 3-10b).

Whereas water table measurements were only available from July 2007, soil moisture was measured for the whole period. There was a weak, but significant, relationship between soil moisture and night-time ER ($R^2 = 0.25$; $p < 0.05$), with fluxes being generally lower under wetter soils (Figure 3-10c). There was an extremely weak, but significant, relationship between soil moisture and the residuals from the ER temperature-dependent model ($R^2 = 0.06$; $p < 0.05$), suggesting that changes in soil moisture may explain a very small proportion of the variation which is not accounted for by the temperature-dependence model (Figure 3-10d).

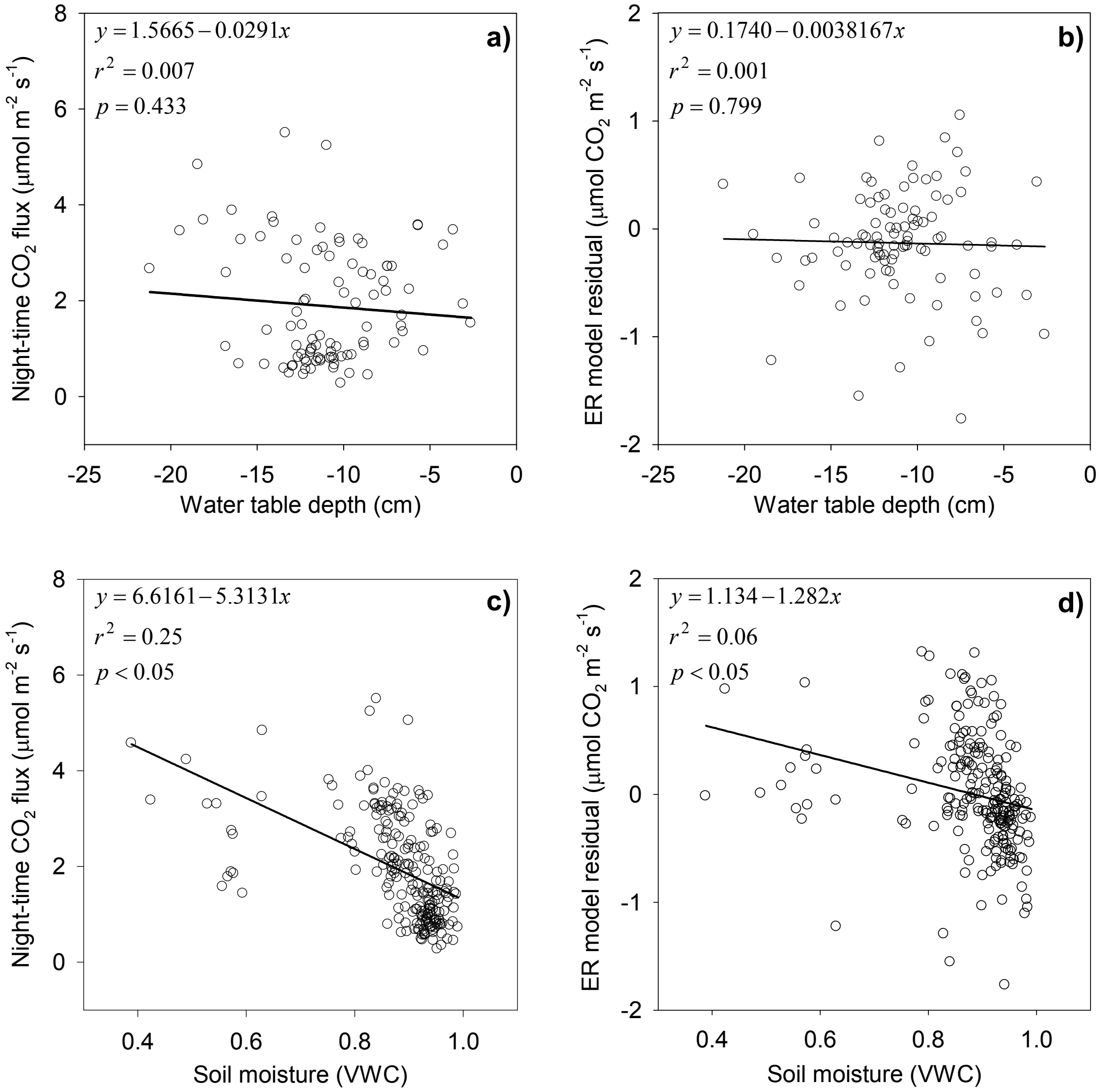


Figure 3-10: a) Relationship between night-time CO$_2$ flux (assumed to be ER) and water table depth. b) Residuals (temperature modelled ER minus observed ER) plotted as a function of water table depth. c) Relationship between night-time CO$_2$ flux and soil moisture. d) Residuals (temperature modelled ER minus observed ER) plotted as a function of soil moisture. All data are night-time means.

3.3.6 Light response relationships

In order to gap-fill day-time NEE fluxes, relationships between day-light hour fluxes and available photosynthetically active radiation were investigated. Vegetation responses to light vary seasonally and with phenological changes and so relationships were developed on a seasonal basis (Figure 3-11). The line in Figure 3-11 show the Photosynthetic Irradiance Response component of Equation 3.3 fitted to the data. The meaningful parameters of the light saturated rate of photosynthesis ($P_{\max}$) and the half-saturation constant (k) which describe the photosynthetic response to light were estimated from these curves for each of the seasonal periods and are shown in Table 3-1. Relationships were stronger during the peak growing season with higher R^2 values of 0.59 for summer months and weaker during the winter when photosynthesis was a far less important component of the day-time NEE flux.

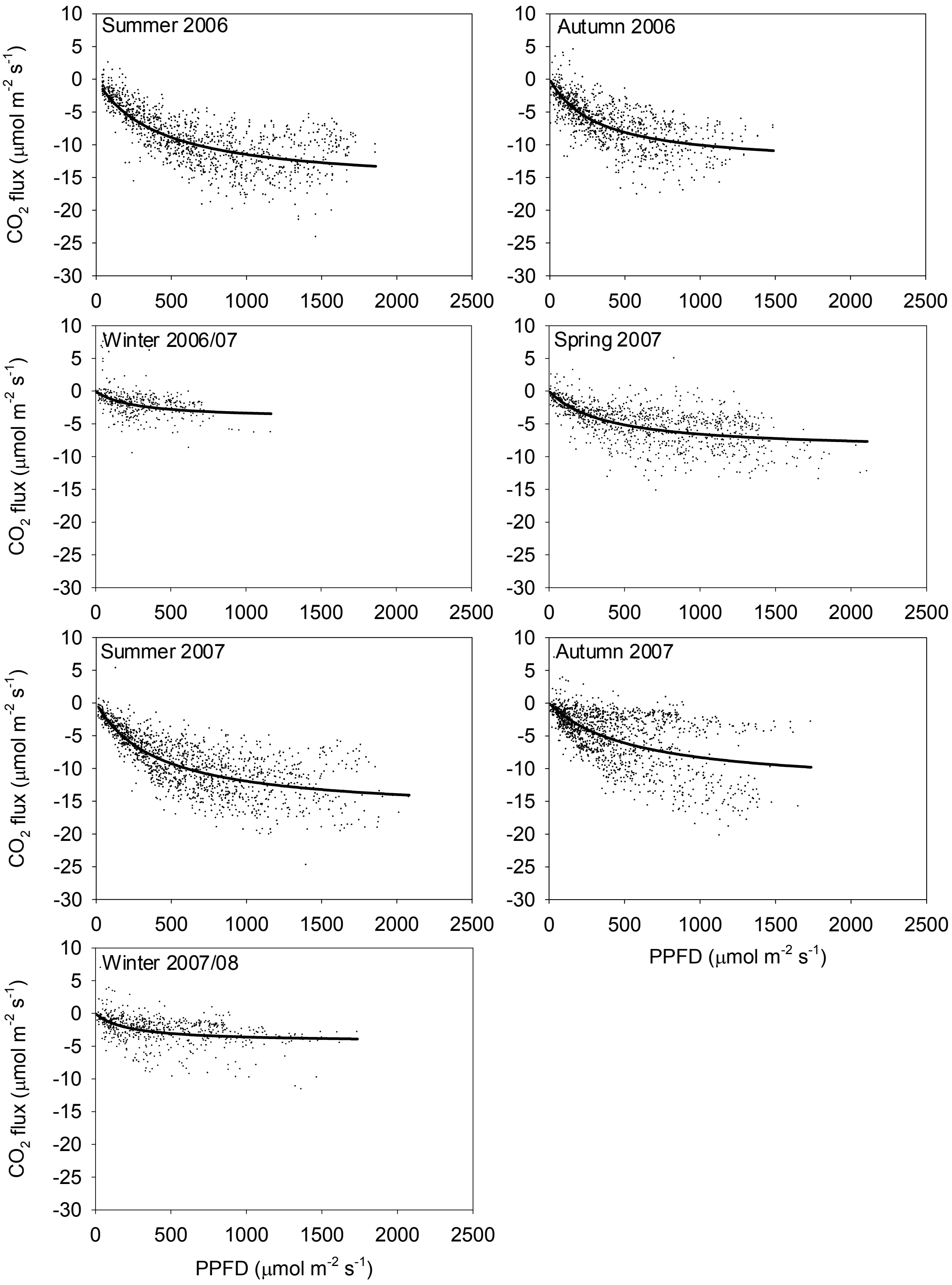


Figure 3-11: Relationship between calculated GPP (measured NEE - calculated ER) and photosynthetic photon flux density (PPFD). Symbols are half-hour data points of calculated GPP; lines show predictions of the photosynthetic irradiance response model fitted to the data. The analysis was carried out separately for seasonal periods and the fitted parameters were used in the gap-filling PIRT model.

Table 3-1: Seasonal parameter values for k (µmol PAR m^{-2} s^{-1}) and P_{max} (µmol CO$_2$ m^{-2} s^{-1}) and associated R^2 values derived from the light response curves presented in Figure 3-11. The parameters were entered into equation 3.3 to model NEE. An indication of the performance of the seasonal models against observed values is shown (RMSE).

Seasonal period	k	P_{max}	R^2	RMSE
Summer 06	416.52	16.27	0.59	2.72
Autumn 06	312.35	13.18	0.50	2.54
Winter 06/07	255.06	4.21	0.16	1.88
Spring 07	378.82	9.07	0.38	2.35
Summer 07	410.63	16.85	0.59	2.75
Autumn 07	565.62	12.98	0.30	2.52
Winter 07/08	217.06	4.39	0.17	1.92

Gaps in the half-hour NEE flux time-series were filled with the PIRT model (Equation 3.3) using the parameters derived from the relationships between observed fluxes and soil temperature (Figure 3-9) and available PAR (Figure 3-11 and Table 3-1). A fully gap-filled time series of half-hour NEE fluxes is presented in Figure 3-12. Model performance is assessed in Figure 3-13 by comparing model predictions to observed NEE from flux tower measurements. A RMSE value of 2.01 µmol m^{-2} s^{-1} was achieved for the whole dataset, which was acceptable considering that the maximum observed fluxes in both directions were relatively high. The model was able to account for nearly 80 % of the variation in observed fluxes and the relationship between observed and modelled fluxes was used to estimate the uncertainty of gap-filled CO$_2$ budgets (see Section 3.3.7).

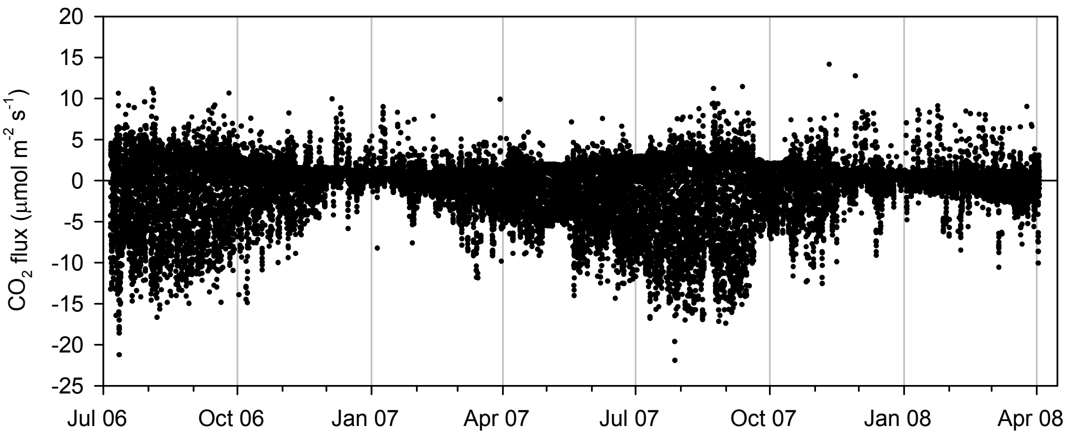


Figure 3-12: Half-hour CO_2 fluxes (µmol m^{-2} s^{-1}) where gaps have been filled using a PIRT model.

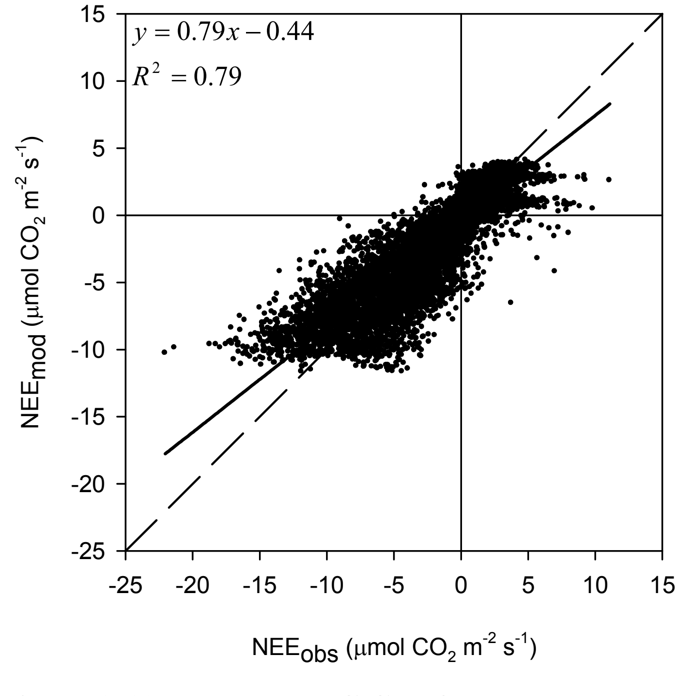


Figure 3-13: Observed EC CO_2 flux versus modelled CO_2 flux for the Bog End flux tower for the whole measurement period. Data points are half-hour EC measurements against the corresponding PIRT model predictions. The best fit linear regression (solid line) and the 1:1 relationship (dashed line) are shown. The RMSE of modelled against observed fluxes was 2.01 µmol m^{-2} s^{-1}.

3.3.7 CO_2 budgets

Using gap-filled data, it was possible to produce daily means of net ecosystem exchange for the whole period, making it easier to identify seasonal trends and transition points (Figure 3-14). In both years, peak daily uptake occurred in July (~4.50 - 5.00 g C m^{-2} d^{-1}) and declined through autumn. The general transition from net daily uptake to net emission occurred around late September/October, although this was not clear cut, with the system periodically switching from small daily sink to source over a period from September to November. The corresponding transition at the start of the growing season occurred in early March, although again there was a degree of switching from source to sink on a daily basis. Peak net emissions of around 1 - 2 g C m^{-2} d^{-1} occurred throughout the winter period.

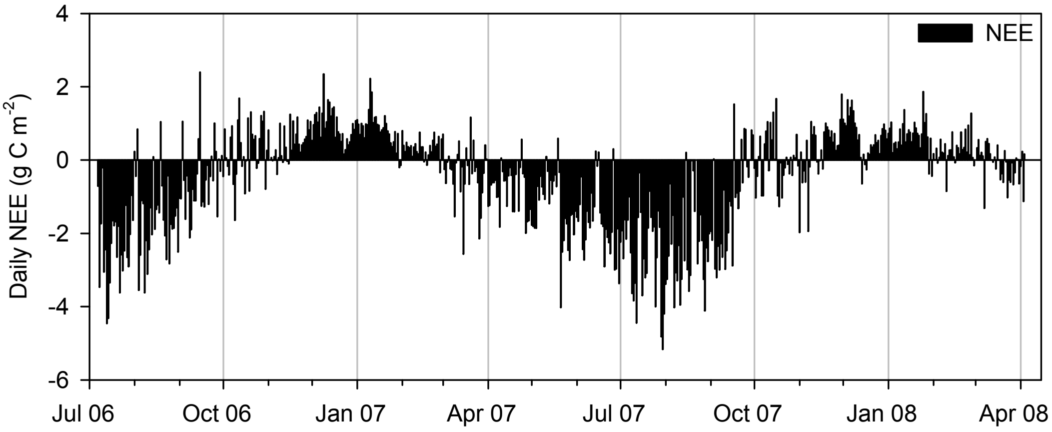


Figure 3-14: Daily NEE (g C m^{-2}) measured at the Bog End flux tower, gaps were filled using a PIRT model. Negative values indicate net uptake, positive values show net emission.

Using the PIRT model, it was possible to partition the measured net flux into its component fluxes and examine how GPP and ER were driving the overall flux on a daily and seasonal basis (Figure 3-15). The model predicts peak daily photosynthetic uptake, or GPP, of 8 g C m^{-2} d^{-1} during July and August with a small amount (< 0.5 g C m^{-2} d^{-1}) of photosynthesis persisting throughout most winter days. The data also revealed that the occasional net release on summer days were a result of sudden decreases in GPP, presumably caused by low available PAR on days with low lying cloud. Flux partitioning suggested that ER reached peaks of around 4 g C m^{-2} d^{-1} during August of both years. As was already apparent from the net fluxes, low levels of ER activity (~1 – 2 g C m^{-2} d^{-1}) continued throughout the winter, driving net emissions to the atmosphere.

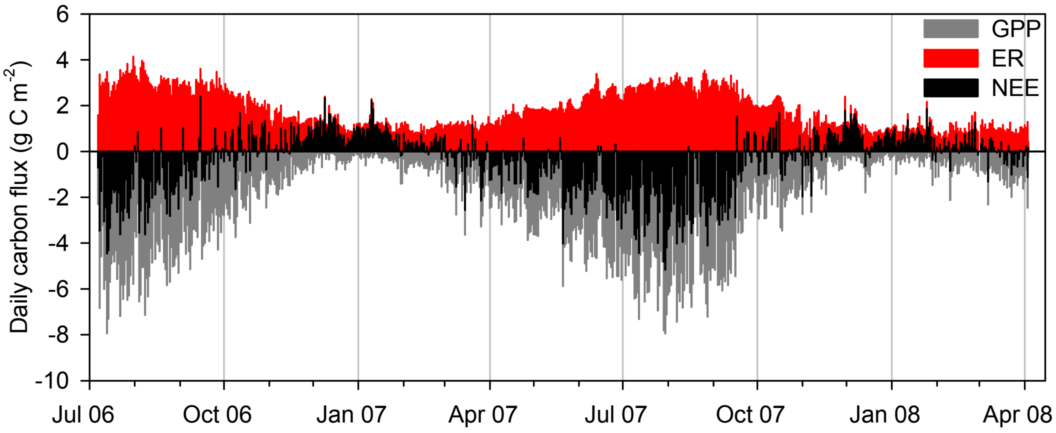


Figure 3-15: Daily fluxes of NEE, GPP and ER (g C m^{-2}) at the Bog End flux tower. Gaps in the NEE record were filled using a PIRT model, which was also used to partition NEE into GPP and ER. Negative values indicate uptake, positive values show emission.

Studying the accumulated flux presented in Figures 3-14 and 3-15 reveals that the site was an overall CO_2 sink of 292 g C m^{-2} during the measurement period; and for the first full year of measurements, the annual budget was 173 g C m^{-2} (Figure 3-16). The results from the flux partitioning exercise showed that this net figure was the balance of an annual CO_2 uptake of 891 g C m^{-2} as GPP and an annual CO_2 loss of 718 g C m^{-2} as ER (Figure 3-16). There was only one complete annual cycle, with measurements ceasing three months short of a second year. However, from the available data, there was a suggestion that the second 12 month period may have been a larger carbon sink, with a cumulative flux of 120 g C m^{-2} after just nine months; the equivalent figure for year one was just 50 g C m^{-2}.

An analysis of the errors associated with the measurement and gap-filling methodologies provided an estimate of the uncertainty associated with the long-term CO_2 balances. Over the full 21 month measurement period, the estimated random error was ± 4.66 % (± 13.65 g C m^{-2}), for the first full year, the figure was ± 4.50 % (± 7.82 g C m^{-2}). After incorporating the larger estimate of systematic errors, the total uncertainty was calculated as ± 18.59 % (292 ± 54.28 g C m^{-2}) for the whole period and ± 18.55 % (173 ± 32.10 g C m^{-2}) for year one.

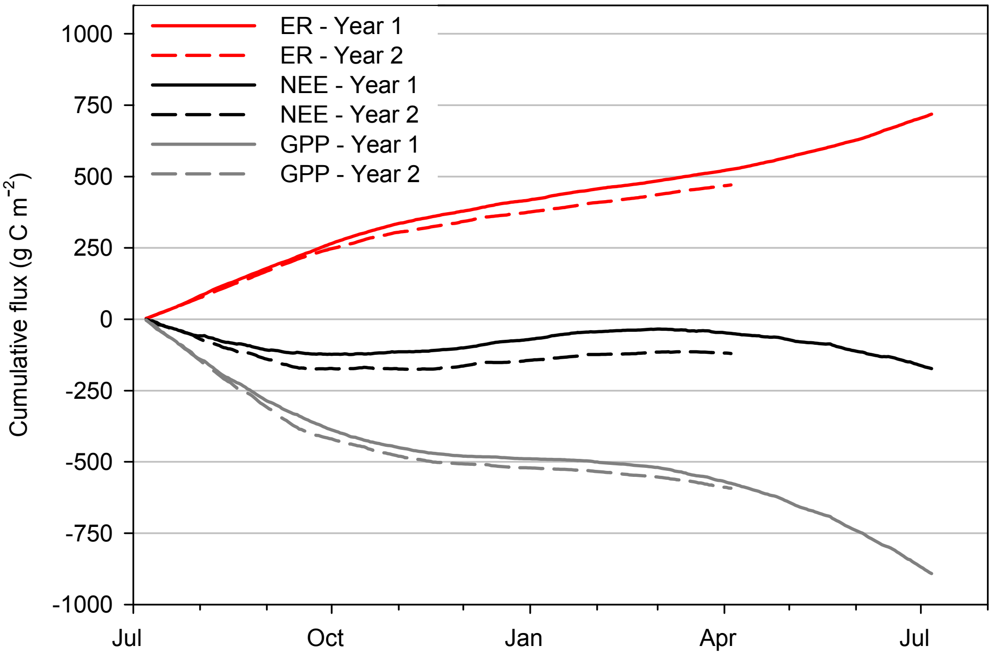


Figure 3-16: Cumulative carbon fluxes (g C m^{-2}) determined from measurements at the Bog End flux tower; negative values indicate uptake. Year one was from July 2006 to June 2007; year two ran from July 2007 to April 2008. NEE includes gap-filled data and NEE was partitioned into GPP and ER using a PIRT model.

Figure 3-17 shows all three fluxes aggregated into monthly totals over the measurement period. July and August were the peak months for both gross primary productivity and ecosystem respiration, however these months also exhibited the greatest net fluxes of CO_2 into the plant-soil system. The winter months of December to February showed the lowest fluxes of GPP and ER but the lowest net fluxes occurred during the transition months when the system was switching from a net sink to source and vice versa

(October in both years and February in 2007 and March in 2008). Winter months made a small contribution to the annual GPP flux (4.5 %), but the period made a much larger and important contribution to the annual ER flux (15.0 %).

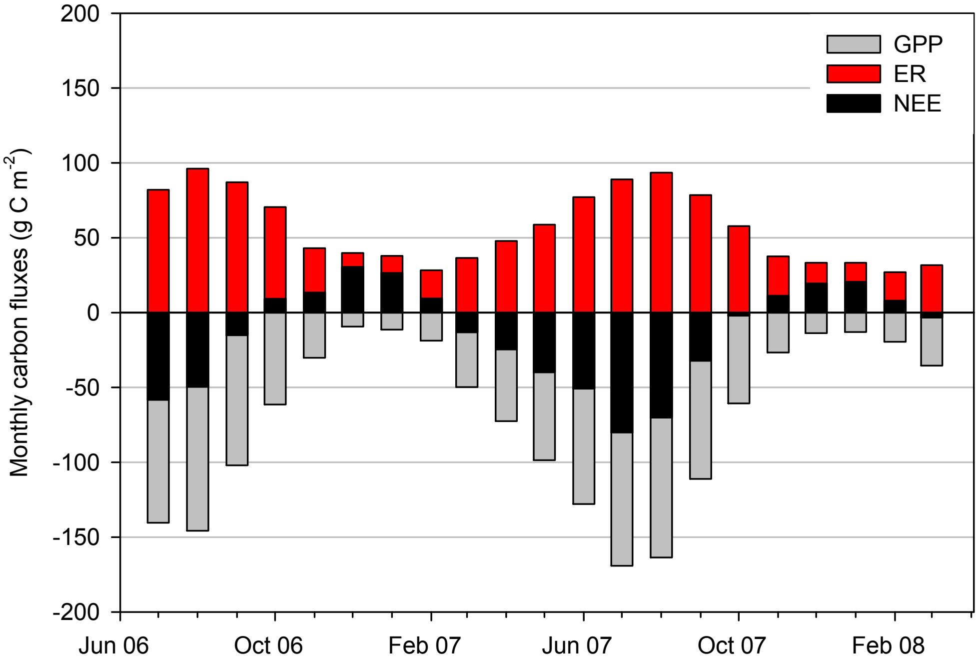


Figure 3-17: Monthly carbon fluxes (g C m^{-2}) determined from measurements at the Bog End flux tower; negative values indicate uptake. NEE includes gap-filled data and NEE was partitioned into GPP and ER using a PIRT model.

3.4 Discussion

3.4.1 Relationships with environmental variables

Because the eddy covariance technique only measures the net flux of CO_2 between the land surface and the atmosphere, this limits the degree to which the data produced can be used to study the effect of environmental variables on the important component fluxes. Night-time has the benefit of only one of the fluxes being active, ecosystem respiration. There was an exponential relationship between night-time CO_2 fluxes and temperature, the relationship with half-hour fluxes showed a reasonable degree of scatter, but when mean night-time values were used, soil temperature was able to explain a high degree of the variation in CO_2 fluxes. A temperature effect on GPP is also predicted as higher temperatures metabolically enhance the rate of photosynthesis up to an optimum after which point the rate of assimilation is expected to decline (Farquhar *et al*., 1980, Melillo *et al*., 1993). However, the effect is difficult to quantify in studies such as this where it is not easy to separate the effects of temperature and available light.

Water table depth was measured at the site for the final nine months of the study, the depth to the water table varied some 20 cm during this period, but for the most part it remained relatively high within a range of 5 to 15 cm below the surface. There was no evidence of water table affecting the measured night-time fluxes. Soil moisture content was measured for the whole measurement period, and so the flux-soil moisture relationship covered a wider range of the conditions found at the site. There was a weak relationship, with fluxes tending to be lower when the peat was wetter, but when the covarying effects of temperature variation were excluded, the apparent relationship became very weak indeed. While soil moisture did fall to relatively low levels of 40 to 60 % VWC, these were rare incidences during the occasional summer dry periods. The peat was consistently close to saturation point for the majority of the period.

In this study, temperature was the main factor explaining variations in night-time CO_2 fluxes and this is also expected to be the case for day-time ecosystem respiration fluxes. A number of other studies have failed to identify strong relationships between water table depth and ecosystem respiration (Smith, 2003, Lafleur *et al*., 2005, Laine *et al*., 2006) but it has been suggested that this might be for different reasons. In the case of the drained New Zealand bog and the continental bog, it has been suggested that the lack of a relationship was due to the fact that the surface peat was constantly above the water table and relatively dry (Smith, 2003, Lafleur *et al.*, 2005). Whilst others have concluded that the absence of any relationship was due to the peat rarely drying out at wetter sites (Updegraff *et al.*, 2001, Laine *et al.*, 2006). Credence is given to this argument by studies which have shown that variation in water table was an important driver of ER during a dry summer but temperature was more important during a wet summer (Bubier *et al.*, 2003, Bubier *et al.*, 2005).

3.4.2 An annual CO_2 budget

The site was found to be a large CO_2 sink, with a net flux of 173 ± 32.10 g C m^{-2} from the atmosphere to the land surface during the first complete 12 months of data (July 2006 to June 2007). A full second years worth of data was not available for a complete assessment of potential interannual variation, however, the cumulated net flux from the following nine months (July 2007 to April 2008) showed a trend towards a larger CO_2 uptake in that second year.

Also working at Moor House, Worrall *et al.* (2003) produced a NEE estimate of 55 g C m^{-2} yr^{-1}. In a later study, the same authors revised their estimates of primary productivity and soil respiration to 123.3 g C m^{-2} yr^{-1} and 107.1 g C m^{-2} yr^{-1} respectively, yielding a net figure of just 16.2 g C m^{-2} yr^{-1} (Worrall *et al.*, 2007). But these estimates which were part of a study quantifying a range of the carbon pathways at Moor House, relied on models which were not calibrated with field measurements from the site itself. The reliance on general relationships between temperature and soil respiration derived from the literature, when these relationships can vary considerably from site to site, will add uncertainty to those estimates.

Studies from comparable ecosystems remain relatively rare, the literature is dominated by studies from sub-arctic tundra and boreal sites (Laine *et al.*, 2007). There is evidence that larger fluxes are possible from peatlands at lower latitudes with an oceanic climate (Table 3-2). Smith (2003) reported a net sink of around 200 g C m^{-2} yr^{-1} from a two year study at an oligotrophic bog with an oceanic climate in New Zealand. The authors speculated that drainage of land surrounding their site had lowered the water table below historical levels, which had favoured increases in gross primary productivity but had affected ecosystem respiration to a lesser degree. A four year time series of measurements from a blanket bog in Ireland confirms that these ecosystems can act as significant CO_2 sinks (96 g C m^{-2} yr^{-1}) but the study also showed a considerable degree of interannual variability with an annual flux of just 26 g C m^{-2} yr^{-1} the following year (Sottocornola and Kiely, 2005, Sottocornola, 2007). Fluxes rather lower than those found in this study have been reported for two peatland sites in Scotland; 41 g C m^{-2} yr^{-1} (Beverland *et al.*, 1996) and 27 g C m^{-2} yr^{-1} (Hargreaves *et al.*, 2003).

Further comparisons are available but these involve studies from continental bogs and those within the boreal zone, where we would expect to find lower fluxes due to cooler temperatures and shorter growing seasons (Table 3-2). Continental bogs also tend to have lower water tables so decomposition rates are likely to be higher than those at a blanket bog (Sottocornola and Kiely, 2005, Laine *et al.*, 2007). The data from a range of sites seem to support this theory with generally lower net CO_2 fluxes from a continental bog (Lafleur *et al.*, 2003), a boreal mire (Sagerfors *et al.*, 2008) and a subarctic mire (Aurela *et al.*, 2004).

Larsen *et al.* (2007) found extremely high net CO_2 uptake of 293 g C m^{-2} yr^{-1} at a temperate heath in Denmark, the study provided evidence that a site with *Calluna* vegetation can sequester significant quantities of CO_2. The plants in their study were believed to be in the ‘building phase’ of its life cycle explaining the extremely high levels of uptake. The study described in this chapter found relatively high carbon uptake rates from blanket bog vegetation, while equivalently high rates of decomposition were likely limited by the generally high water table and often saturated peat (Table 3-3).

Table 3-2: Annual CO_2 budgets (g C m^{-2} yr^{-1}) for Moor House and range of peatlands and other similar ecosystems for comparison. Most studies used a combination of eddy covariance data and models to obtain annual sums.

Ecosystem	Site	Location	Lat/Long	CO_2 balance	Time period	Reference
Raised bog	Moanatuatua	New Zealand	37 45 S, 175 20 E	-185	1999	(Smith *et al.,* Smith, 2003)
				-210	2000	
Ombrotrophic bog	Mer Bleue	Southeast Canada	45 40 N, 75 50 W	-76	1998-1999	(Lafleur *et al.*, 2003)
				-69	1999-2000	
				-68	2000-2001	
				-10	2001-2002	
Blanket bog	Glencar	Southwest Ireland	51 55 N, 9 55 W	-66	2002-2003	(Sottocornola and Kiely, 2005)
				-65	2003-2004	
				-96	2004-2005	(Sottocornola, 2007)
				-26	2005-2006	
Grassland	Glencar	Southwest Ireland	51 55 N, 9 55 W	-277	2003-2004	(Lawton *et al.*, 2006)
Blanket bog	Moor House	Northern England	54 41 N, 2 21 W	-173	2006-2007	This study
Ombrotrophic bog	Auchencorth Moss	Southeast Scotland	55 47 N, 3 14 W	-27	1995-1996	(Hargreaves *et al.*, 2003)
Bog	Fäjemyr	Southern Sweden	56 15 N, 19 33 E	-22	2005-2006	(Lund *et al.*, 2007)
Temperate heath	Mols Bjerge	Denmark	56 23 N, 10 57 E	-293	2004-2005	(Larsen *et al.*, 2007)
Ombrotrophic bog	Strathy Bog	Northwest Scotland	58 27 N, 4 06 W	-41	1992	(Beverland *et al.*, 1996)
Minerotrophic mire	Degerö Stormyr	Northern Sweden	64 11 N, 19 33 E	-48	2001	(Sagerfors *et al.*, 2008b)
				-61	2002	
				-56	2003	
				-55	2004	(Nilsson *et al.*, 2008)
				-48	2005	
Tundra	Kolyma river	Northeast Siberia	68 37 N, 161 20 E	-38	2003	(Corradi *et al.*, 2005)
Minerotrophic mire	Kaamanen	Northern Finland	69 08 N, 27 17 E	-4	1997	(Aurela *et al.*, 2004)
				-21	1998	
				-8	1999	
				-6	2000	
				-37	2001	
				-53	2002	
High Arctic	Ny-Ålesund	Svalbard	78 56 N, 11 55 E	-9	1995	(Lloyd, 2001)

Table 3-3: Literature values of peak season day and night-time net CO_2 fluxes (µmol m^{-2} s^{-1}) for Moor House and range of peatlands and other similar ecosystems for comparison.

Ecosystem	Site	Location	Lat/Long	Daytime uptake peak season	Night time emissions peak season	Reference
Raised bog	Moanatuatua	New Zealand	37º 45’ S, 17º 20’ E	-10.00	5.00	(Smith *et al.,* Smith, 2003)
Ombrotrophic bog	Mer Bleue	Southeast Canada	45º 40’ N, 75º 50’ W	-10.23	4.55	(Lafleur *et al.*, 2003)
Blanket bog	Moor House	Northern England	54º 41’ N, 02º 21’ W	-15.00	7.00	This study
Extreme rich fen	Alberta	Southwest Canada	54º 47’ N, 113º 32’ W	-5.00	2.00	(Glenn *et al.*, 2006)
Ombrotrophic bog	Auchencorth Moss	Southeast Scotland	55º 47’ N, 03º 14’ W	-8.33	5.56	(Hargreaves *et al.*, 2003)
Poor fen	Alberta	Southwest Canada	55º 54’ N, 112º 33’ W	-5.00	2.00	(Glenn *et al.*, 2006)
Boreal fen	Manitoba	Canada	55º 09’ N, 98º 4’ W	-4.55	2.27	(Lafleur *et al.*, 1997)
Bog	Fäjemyr	Southern Sweden	56º 15’ N, 19º 33’ E	-7.95	5.68	(Lund *et al.*, 2007)
Temperate heath	Mols Bjerge	Denmark	56º 23’ N, 10º 57’ E	-20.00	10.00	(Larsen *et al.*, 2007)
Ombrotrophic bog	Strathy Bog	Northwest Scotland	58º 27’ N, 4 º 06’W	-8.00	3.00	(Beverland *et al.*, 1996)
Low Arctic tundra	Daring Lake	Northwest Territories	64º 52’ N, 111º 34’ W	-6.00	3.00	(Lafleur and Humphreys, 2008)
Minerotrophic mire	Kaamanen	Northern Finland	69º 08’ N, 27º 17’ E	-4.55	2.27	(Aurela *et al.*, 2004)
High Arctic	Ny-Ålesund	Svalbard	78º 56’ N, 11º 55’ E	-1.00	0.50	(Lloyd, 2001)

3.1.1 Comparison to estimates of long-term carbon accumulation

The results presented in this chapter suggested a carbon accumulation as a result of net CO_2 exchange of 173 ± 32.10 g C m^{-2} yr^{-1}. This can be compared to the long-term rates of carbon accumulation at the site obtained by independent estimates. However, there are significant pathways by which carbon can be gained and lost from the system, which were not measured as part of this study. Worrall *et al.* (2007) provided estimates of the magnitude of some of these fluxes (see Table 3-4). These pathways constitute a loss of 38.44 g C m^{-2} yr^{-1}, which reduces the estimate of total carbon accumulation to 134.56 ± 32.10 g C m^{-2} yr^{-1}.

Table 3-4: A summary of carbon uptake and release estimates for components of the carbon cycle at Moor House, produced by Worrall *et al.* (2007).

Pathway	Value (g C m^{-2} yr^{-1})	Source
Methane	3.88	(Worrall *et al.*, 2003) [a]
Rainfall dissolved organic carbon	-2.91	ECN monitoring
Rainfall dissolved inorganic carbon	-3.03	ECN monitoring
Particulate organic carbon	19.90	(Worrall *et al.*, 2003) [b]
Dissolved organic carbon	14.40	ECN monitoring
Dissolved CO_2	6.20	(Worrall *et al.*, 2007) [c]
Total	38.44	

[a] Modelled by an empirical relationship between methane flux and water table derived from the literature.
[b] Estimated from storm sampling.
[c] Modelled based on estimates of soil CO_2 flux.

Hardie *et al.* (2007) investigated the issue using bomb ^{14}C at a number of blanket bog plots at Moor House. Sampling the top 16 cm of the peat profile, they found considerable variation in both the calculated peat growth rate and carbon accumulation rate between the six cores, which had been collected from a 57.5 m^2 plot with homogenous vegetation cover. The rate of peat growth was found to range from ~0.08 to 0.32 cm yr^{-1}, and the overall range of carbon accumulation was between ~20 and ~125 g C m^{-2} yr^{-1}. An obvious question to pose is: how do these estimates of current or recent annual carbon accumulation fit with the amount or depth of peat that is present at the site today? Such a calculation requires estimates of bulk density and the carbon content of peat dry matter, both of which vary with peat depth. Typically the carbon content of peat is between 45 and 50 % of dry matter and peat bulk densities at Moor House vary from 0.04 to 0.14 g cm^{-3} (Jones and Gore, 1978, Hardie *et al.*, 2007). These figures yield an estimate of 0.15 to 0.37 cm yr^{-1} as the annual increase in peat depth, based on annual carbon balance presented in this chapter. This is at the higher range or above the long-term accumulation estimates produced for other similar Moor House sites using different methodologies. Johnson & Dunham (1963) identified the sub Atlantic/sub Boreal transition in the pollen record at two Moor House sites close to Bog End (Bog Hill and Valley Bog) and showed long-term accumulation rates of between 0.03 and 0.12 cm yr^{-1} (Table 3-5). Further evidence was provided by ^{14}C dating in the 1970s, suggesting rates of between 0.03 and 0.06 cm yr^{-1}. If the annual rates of increase based on this study had been constant for several thousand years, we could expect an accumulated peat depth of between 300 and 900 cm over 2500 years, compared to 70 - 100 cm of accumulation estimated for a similar site using the pollen record. The pollen record suggests that greater accumulation (200 – 300 cm) did occur during the last 2500 years, but this was found at wetter sites with deeper total peat deposits than at Bog End (Table 3-5).

Table 3-5: A comparison of estimates of long-term peat accumulation (cm) and average accumulation rates (cm yr^{-1}) for a range of sites at Moor House, calculated with a variety of methods including figures based on carbon fluxes calculated in this chapter.

Site	Long-term peat accumulation (cm)	Average accumulation (cm yr^{-1})	Source
Bog Hill	70 – 100 cm (2500 yrs)	0.03 – 0.04	Pollen record (Johnson and Dunham, 1963)
Valley Bog	200 – 300 cm (2500 yrs)	0.08 – 0.12	Pollen record (Johnson and Dunham, 1963)
Sike Hill	56 – 80 cm (2500 yrs)	0.02 – 0.03	Pollen record (Jones and Gore, 1978)
Sike Hill	50 cm (1422 ± 110 yrs)	0.03 – 0.04	^{14}C dating (Jones and Gore, 1978)
Green Burn	200 – 300 cm (2500 yrs)	0.08 – 0.12	Pollen record (Jones and Gore, 1978)
Green Burn	150 cm (3052 ± 90 yrs)	0.05 – 0.06	^{14}C dating (Jones and Gore, 1978)
Hard Hill	–	0.08 – 0.32	Bomb ^{14}C dating (Hardie *et al.*, 2007)
Bog End	–	0.15 – 0.37	This study

It is a difficult exercise to reconcile these two methods of accounting for rates of peatland carbon accumulation. In general, it appears that the present day carbon balance is resulting in the bog accumulating more carbon per year than the long-term average for the site. Certainly, simple calculations suggest that if the current measured net carbon inputs have been a long-term feature of the bog, then there should be deeper peat deposits than are currently found at the site. However, it is notable that Hardie *et al.*'s (2007) bomb ^{14}C study, which was based on accumulation over the more recent past (~50 years), although variable, included some estimates not dissimilar to those found in this study. It is also necessary to reiterate the relatively short-term nature of this study period. While with caution it is possible to compare long-term accumulation rates with those measured for the study period; as there will be some inter-annual variability it is not possible to say how representative the study period was of the contemporary carbon balance. A number of other studies have attempted to compare contemporary measurements with longer-term peat profile records. Roulet *et al.* (2007) found good agreement between long-term late Holocene (400-3000 BP) carbon accumulation (21.9 ± 2.8 and 14.0 ± 37.6 g C m^{-2} yr^{-1} for two cores) and the mean carbon balance of six years of data (-21.5 ± 39.0 g C m^{-2} yr^{-1}) at Mer Bleue bog in Canada. Working on a New Zealand raised bog, Smith (2003) found contemporary annual carbon sequestration (198 g C m^{-2} yr^{-1}) to be approximately six times greater than the long-term average (34 g C m^{-2} yr^{-1}). The author suggest that the difference may result from the contemporary measurements not accounting for carbon losses to the atmosphere during the relatively frequent fires, they also hypothesise that recently lowered water tables have perturbed the system stimulating carbon uptake through higher GPP and plant growth.

3.2 Summary

The eddy covariance technique was utilised to make half-hourly measurements of the net CO_2 flux over an area of blanket bog at Moor House. Measurements were made over a 22 month period between July 2006 and April 2008.

Through measurements and modelling the site was shown to be a significant carbon sink over the measurement period and an annual cycle of 173 ± 32.10 g C m^{-2}. There was considerable seasonal variation with the site acting as a net CO_2 source during the winter months (five months in 2006/07 and four in 2007/08).

The net CO_2 flux was separated into its components, gross primary productivity and ecosystem respiration. A flux partitioning routine was employed by estimating day-time ecosystem respiration based on relationships between night-time fluxes and soil temperature.

There was an estimated 20 % offset between carbon fixed through GPP and carbon respired as ER, this represents the estimate of net CO_2 sequestration by the vegetation and soils over one year.

Soil temperature best explained the variations in half-hourly and mean night-time ecosystem respiration fluxes. Water table did not appear to play a role; there was a suggestion of a very weak relationship between ecosystem respiration and soil moisture.

A full assessment of potential interannual variability was not possible because measurements stopped several months short of a complete second year. Nevertheless, there was evidence that the second year was on course to exhibit a larger CO_2 sink than year one; comparing the cumulative flux after nine months, the net uptake was 60 % higher.

CHAPTER 4

COLLAR INSERTION AFFECTS SOIL CO_2 FLUX MEASUREMENTS

4.1 Introduction

4.1.1 The soil CO_2 flux

The flux of CO_2 from soils is an important component of net ecosystem exchange and the carbon balance of most ecosystems as a whole (Luo & Zhou, 2006; Raich & Schlesinger, 1992). Whilst the process and its role in the carbon cycle at Moor House are examined in detail in the following chapter; this chapter concentrates on testing a commonly applied methodology of measuring these fluxes. However, a brief consideration of the process in a peatland system, such as Moor House, is appropriate here. It is a relatively complex pathway, itself being made up of several processes, which, are variously described in the literature as either being discrete or highly related. A distinction is made between the terms, soil respiration and soil CO_2 flux. Soil respiration can be defined as "the total CO_2 production in intact soils resulting from the respiration of soil organisms, roots and mycorrhizae" (Raich & Schlesinger, 1992); whilst the soil CO_2 flux is what we commonly measure in the field and comprises CO_2 production but is also affected by the rate of transfer of CO_2 to the surface. Raich & Schlesinger (1992) suggest that on an annual basis the two processes are approximately equal, but may vary significantly over shorter timescales. Consequently, in this chapter measurements are referred to as soil CO_2 fluxes.

In the definition, the flux is composed of the products of respiration of three main organism types and it is useful to partition the flux accordingly. The term autotrophic respiration is applied to root respiration; whilst respiration by microbes and soil fauna is termed heterotrophic respiration. In reality, however, the situation is rather more complex, with roots often providing the exudate material which goes on to form the basis of heterotrophic respiration, whilst it is not clear into which definition mycorrhizal respiration fits and there is some debate in the literature about these points (Högberg *et al.*, 2006; Kuzyakov, 2006a, b). For the purposes of this study it is noted that it is useful to think in terms of partitioning, as fluxes from different sources will likely respond to environmental variables in different ways. Further, in an ecosystem where roots are concentrated in the litter and upper soil layers, there is the possibility of affecting differentially the flux processes when measurement techniques disturb this part of the soil profile.

4.1.2 A measurement problem

A key concern of any experiment is the degree to which the very act of observing or measuring a phenomenon does itself affect the phenomenon. This is a widely acknowledged problem associated with chamber-based methods of measuring soil CO_2 fluxes, where placing a chamber over a patch of soil has the potential to significantly alter the environmental conditions that are driving the CO_2 flux. Some of the main potential problems are: distortion of the CO_2 diffusion gradient; differential pressure gradients inside and outside the chamber and temperature and soil moisture effects. In commonly used systems, these effects have been minimised as far as possible, for example, measurement times are kept short in order to minimise the build up of CO_2 and altered diffusion gradients. Short closure times will also reduce any soil temperature or soil moisture effects caused by covering the soil. Finally, innovative vent designs applied to modern chamber systems allow chamber pressure to equilibrate with that of ambient air (Xu *et al.*, 2006). While these factors have been identified and researched in detail, the potential disturbance of inserting collars into the soil has received little attention, with an extensive search of the literature, revealing just one study investing this issue (Wang *et al.*, 2005). Working in a larch forest (*Larix gmelinii*) in China, they found a decrease in the soil CO_2 flux with increasing depth of collar insertion. However, their study was based on a limited data set of just one measurement point in time.

Permanent collars are an integral part of most chamber designs and are a feature introduced in order to reduce the disturbance effect of repeatedly placing a chamber directly onto the soil surface. They further act to create a seal between the soil surface and the chamber. A recent detailed review of the literature (Heinemeyer *et al.*, unpublished data) found that the mean collar insertion depths reported in soil respiration experiments were: 7.0, 16.3 and 6.0 cm in tundra/shrubland, northern peatlands and tropical peatlands respectively; in some cases, collars were inserted to a depth of 30 cm.

An analysis of root distributions for terrestrial biomes showed that tundra, boreal forest and temperate grasslands exhibited shallow rooting profiles, with 80-90 % of roots found in the top 30 cm of soil (Jackson *et al.*). Peatlands with high water tables would be expected to have particularly shallow profiles, with roots concentrated in the more aerated upper layers. Backeus (1990) reported a study at a Swedish ombrotrophic mire, which found more than 50 % of the fine roots grown over a year were located in the top 10 cm of peat. There was also evidence that this distribution with depth was dependent on the depth to the water table. Simple observations of the vegetation and soils at Moor House suggested that a high proportion of the live roots were contained within the uppermost layers of the peat. It seems likely therefore, that inserting a collar down through this rooting zone will sever a large proportion of live roots and lead to a reduction on the autotrophic component of respiration and an underestimation of the true soil CO_2 flux.

In this chapter the results of a detailed study of the root distribution are presented. These findings are then related to an experiment which aimed to test the effect on measured soil CO_2 fluxes of inserting collars through the rooting zone.

4.2 Methods

4.2.1 Field site

The experiment was conducted at the Bog End area of the Moor House reserve (54° 41’ 27” N, 02° 21’ 50” W; 564 m elevation). The site is described in detail in Section 2.4 and measurement plots were established 5 m to the north of the eddy covariance flux tower described in Chapter 3.

4.2.2 Chamber CO_2 measurements

Soil CO_2 fluxes were measured using a LI-8100 closed dynamic chamber system (LI-COR, Lincoln, Nebraska, USA). The system could either be used with the IRGA and a single survey chamber (Model 8100-103) to make manual measurements or attached to 16 long-term chambers (Model 8100-101) for continuous monitoring via a custom built multiplexer unit (Electronics Workshop, Biology Department, University of York, UK). Both chamber designs had a 20 cm diameter with chamber volumes of 4.84 L (survey chamber), 4.09 L (long-term chambers) and a flow rate of 1.5 L min^{-1}. Collars of 20 cm diameter and constructed from PVC drain pipe material were installed at each plot (Figure 4-1). The degree to which collars were inserted into the peat was dependant upon the treatment (See 4.2.3 Experimental design), but in all cases, collars extended 14 cm above the surface of the peat. During measurements, chambers were placed over the collars, with a rubber gasket maintaining the seal. The CO_2 flux was calculated as the linear increase in CO_2 concentration based on one second measurements during a chamber closure period of 1 – 2 minutes (Heinemeyer *et al.*, 2007). The measurements from the initial 20 s form a ‘dead band’, while steady mixing is achieved within the system, and were not used to calculate fluxes.

4.2.3 Experimental design

Sixteen 20 cm diameter plots were identified in September 2006 which were contained within a 150 m^2 area of blanket bog. Plots were chosen to be amongst uniform vegetation cover, by selecting locations next to *Calluna* plants. In a pre-treatment period all sixteen plots soil CO_2 fluxes were measured in the same way, using a manual survey chamber and surface collars. Based on the results of three surveys, plots were ranked in terms of the average magnitude of the measured fluxes and assigned to one of four blocks ranging from highest to lowest fluxes. Four treatments were then randomly assigned to the plots within each block. The LI-8100 automated chamber system was installed on 05 October 2006, again using surface collars over all plots to observe pre-treatment conditions.

On 09 October 2006, the collar depth treatments were applied as follows: 1) fluxes measured in the same way as the pre-treatment control, with surface collars; 2) collars inserted 5 cm into the peat; 3) collars inserted 10 cm and 4) collars inserted 20 cm (Figure 4-2). Surface collars were placed on the surface and held down by the weight of the chambers and stainless steel rods (2.5 mm diameter welding rods) which were inserted into the peat to a depth of 30 cm. When collars were inserted, a sharp knife was used to pre-cut the peat to a target depth, to limit disturbance and compaction. The automated chamber system, taking hourly measurements during the post-treatment phase, remained in place until 19 October 2006. After this point, the system was required to continue long-term monitoring of other plots at Moor House (see Chapter 5) and thereafter was unavailable to this project. However, the plots were maintained and at various points measurements were carried out using the survey chamber to study the longer-term effects (29 November 2006, 05 December 2006, 29 August 2007, 03 September 2007 and 21 July 2008).

All inserted collars were removed on 21 July 2008 to investigate the potential effects of draining water-logged plots; plots were subsequently monitored using surface collars (21 July 2008, 25 July 2008 and 28 July 2008). Finally, on 28 July 2008, the peat around all plots was cut to a depth of 20 cm, to simulate the root cutting effect of collar insertion, but without the potential for affecting drainage within the plots. Survey chamber measurements were taken on 11 August and 22 August 2008 to monitor this effect.

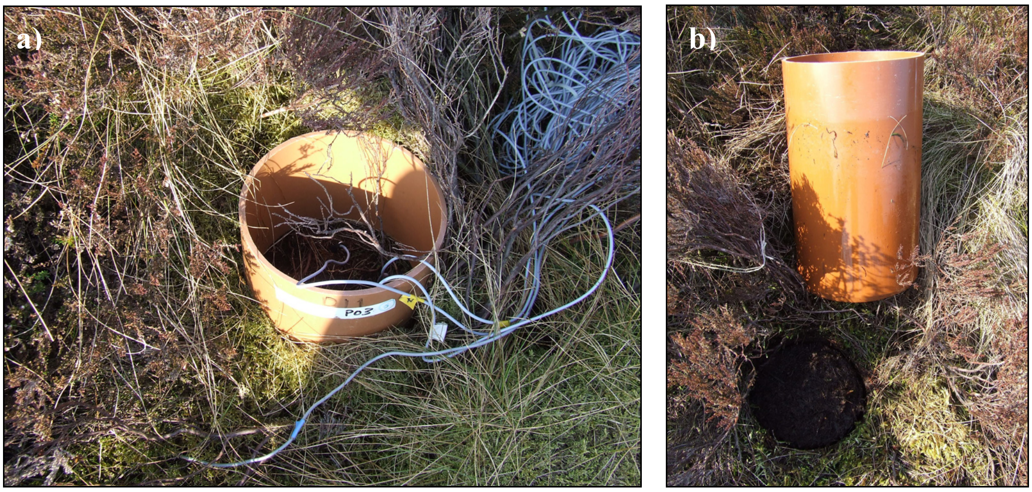


Figure 4-1: Photographs of measurement collars a) *in-situ*, either manual survey or long-term automated chambers fit around the collars; b) an example of a 20 cm collar removed from its inserted position.

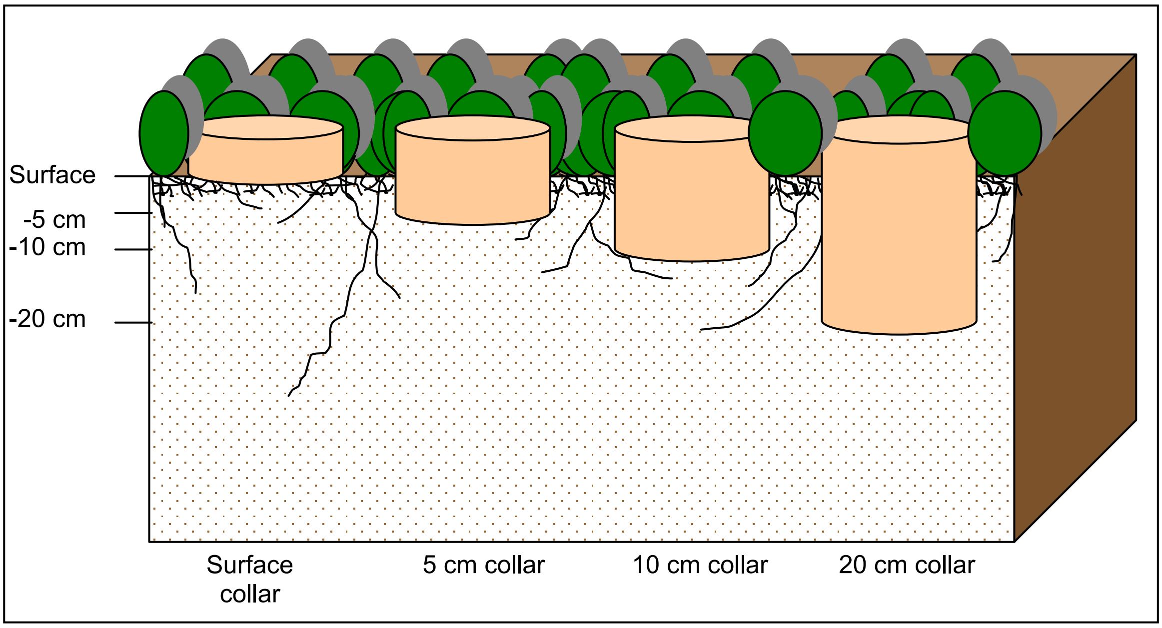


Figure 4-2: A schematic representation of the four collar depth treatments in the experiment. Collars were placed in natural gaps between *C. vulgaris* plants and any green vegetation was clipped back such that only the soil CO_2 fluxes were being measured. Surface collars were pressed down onto the litter layer, while the other treatments saw collars being inserted into the peat to depths of 5 cm, 10 cm and 20 cm below the surface.

4.2.4 Other measurements

The experimental site was within 5 m of the eddy covariance flux tower, so the full range of climate and environmental measurements described in Chapter 3 were available to this study. Briefly, these included, air temperature, relative humidity, wind speed and direction, net radiation, photosynthetically active radiation, soil temperature and soil moisture. Precipitation and solar radiation data were again available from the ECN weather station, approximately 750 m from the study site and at a similar altitude.

4.2.5 Analysis of root distribution

Three peat cores were extracted from the bog on 27 November 2006 using a 6 x 6 cm square peat corer, at a distance of approximately 10 m from the experimental site, but amongst similar vegetation. The cores were stored for one week at 4°C, after which, each core was divided into depth segments (0.0 to 5.0 cm; 5.0 to 10.0 cm and 10.0 to 20 cm) and live roots were extracted by placing the core segments in trays of water and picking out live roots based on appearance, colour and flexibility. For the top two segments, a considerable amount of very fine root matter remained at the bottom of the tray after the larger roots had been removed. The base of the tray was divided into 12 squares and one was randomly selected for a thorough analysis of these fine roots and the data obtained for that square upscaled to the whole tray area. Root material was scanned and high resolution images were analysed (WinRhizo®; Régent Instruments, Quebec, Canada) to determine root length and average root diameter per core depth segment. Root dry weight (DW) was recorded after oven drying for 3 days at 65°C to constant weight.

4.2.6 Statistical analysis

For the period of continuous monitoring, daily mean CO_2 fluxes were compared by using one-way repeated measures analysis of variance (ANOVA) with between subjects comparisons. One-way ANOVA with post-hoc comparison was used to compare treatment means of survey measurements of CO_2 fluxes, soil temperature and soil moisture. In cases where the requirements for ANOVA were not met, a non-parametric alternative, Kruskal-Wallis test was performed instead. One-way ANOVA with post hoc comparison was also used to compare differences in mean root length and mass at different peat depths. The significance of correlations between fluxes and environmental variables was tested by using linear regression, with *p* values of < 0.05 considered statistically significant. All data analysis was performed with SPSS version 12.0.1 (SPSS Inc, Chicago, Illinois).

4.3 Results

4.3.1 Collar depth affects the magnitude of the soil CO_2 flux

Pre-treatment monitoring of soil plots during September and early October 2006, with both manual survey measurements (Figure 4-3) and continuous hourly monitoring (Figure 4- 4), showed no significant differences in soil CO_2 fluxes between 'treatment' blocks ($p > 0.05$).

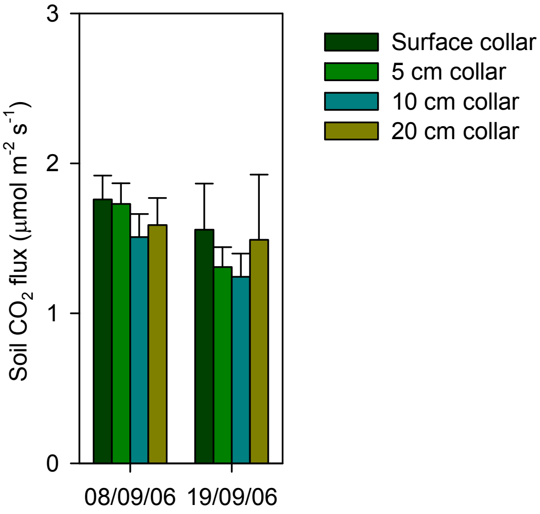


Figure 4-3: Mean soil CO_2 fluxes (µmol m^{-2} s^{-1}) measured using the manual survey chamber. Each bar represents the treatment mean (n = 4) and error bars show + one standard error. During this pre-treatment phase of the experiment, surface collars were used to measure the fluxes over all plots and there were no significant differences between 'treatments' ($p > 0.05$). 08/09/06: $F = 0.492$; d.f. = 3; $p = 0.695$. 19/09/06: $F = 0.322$; d.f. = 3; $p = 0.810$.

Figure 4-4 shows detailed hourly CO_2 flux data for the period of continuous monitoring. During the pre-treatment period (05 October to 09 October 2006), fluxes vary over time from a minimum of 0.5 µmol m^{-2} s^{-1} to a maximum of 1.5 µmol m^{-2} s^{-1}. While there is evident natural variation in the magnitude of the fluxes, during this period when all plots were measured with surface collars, there are no obvious 'treatment effects'. Treatments were applied on the morning of 09 October, when collars were inserted as required between 10:00 and 13:00 and hourly monitoring of CO_2 fluxes resumed immediately. Following this, there was a pronounced decline in soil CO_2 flux from all treatments, which was likely to be a result of a sudden drop in temperature over night. The first evidence of a collar depth treatment effect occurred by 06:00 the following morning. Fluxes increased under all treatments, but this was much more pronounced in the surface collar treatment. Throughout the period of continuous monitoring, fluxes were consistently higher from the surface collar treatment than from any of the inserted collar treatments. During the course of the ten subsequent days, mean daily fluxes were between 39 – 52 % lower from the 5 cm collar treatment; 36 – 56 % lower from the 10 cm collar treatment; and 41 – 65 % lower from the 20 cm collar treatment compared to fluxes from the surface collar treatment.

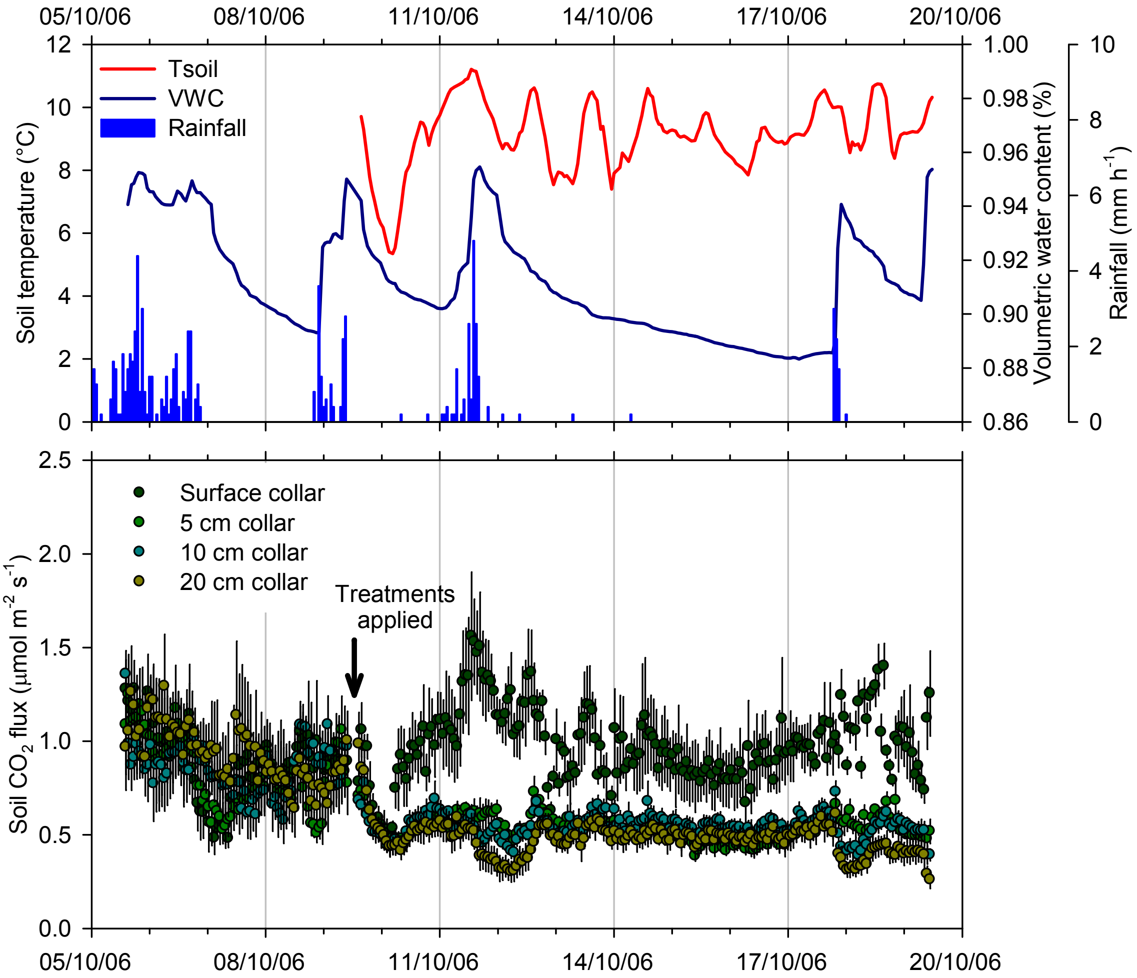


Figure 4-4: Mean hourly soil CO_2 fluxes (µmol m^{-2} s^{-1}) measured using automated chambers ($n = 4$), bars represent ± one standard error. The plot shows an initial pre-treatment period (05 to 09 October 2006) when all plots were measured using surface collars. On the 09 October four plots were assigned to each of the collar depth treatments (surface; 5 cm; 10 cm and 20 cm) and collars were inserted as required. Hourly measurements continued up until 19 October. Analysis comparing daily means showed that fluxes from inserted collar treatments were significantly lower than from the surface collar treatment ($p < 0.05$). The top panel shows soil temperature, soil moisture and rainfall events for the same period.

The effect of collar insertion on daily mean CO_2 fluxes during the period of continuous monitoring was tested using between-subjects repeated measures ANOVA across the following ten days (pre-treatment period: 06 October and post-treatment period: 11 to

19 October 2006). There was no significant interaction between collar depth treatment and time, Wilks Lambda = 0.011, *F* (27, 12) = 1.698, *p* = 0.165. There was a significant main effect for time, Wilks Lambda = 0.043, *F* (9, 4) = 9.866, *p* = 0.021, with inserted collar treatments showing a reduction in mean daily CO_2 fluxes. The main effect comparing the four collar depth treatments was significant, *F* (3, 12) = 8.162, *p* = 0.003, showing that there were differences in CO_2 fluxes between treatments over the period of continuous monitoring. A post-hoc test confirmed that this was due to significantly higher fluxes from the surface collars compared to all three of the inserted collar treatments (surface collars compared to: 5 cm collars, *p* = 0.024; 10 cm collars, *p* = 0.031; 20 cm collars, *p* = 0.002). The mean fluxes from the three inserted collar treatments were not significantly different from one another, $p > 0.05$ in all cases.

4.3.2 Effects on environmental relationships

There were considerable differences in the responses of soil CO_2 fluxes to driving variables such as temperature. Soil temperature was better able to explain the variation in soil CO_2 fluxes measured using surface collars. The fluxes measured from deeper collar treatments were less dependent on soil temperature as a driving variable (Figure 4-5). Further, when these relationships were used to estimate the temperature sensitivity of the soil CO_2 flux, there was an apparent treatment effect, with a Q_{10} of 3.62 estimated from the surface collar data compared to a value of 1.63 from the 5 cm collars. The relationships between the fluxes from the deeper collar treatments (10 and 20 cm) and temperature were too poor to be used to estimate Q_{10} responses.

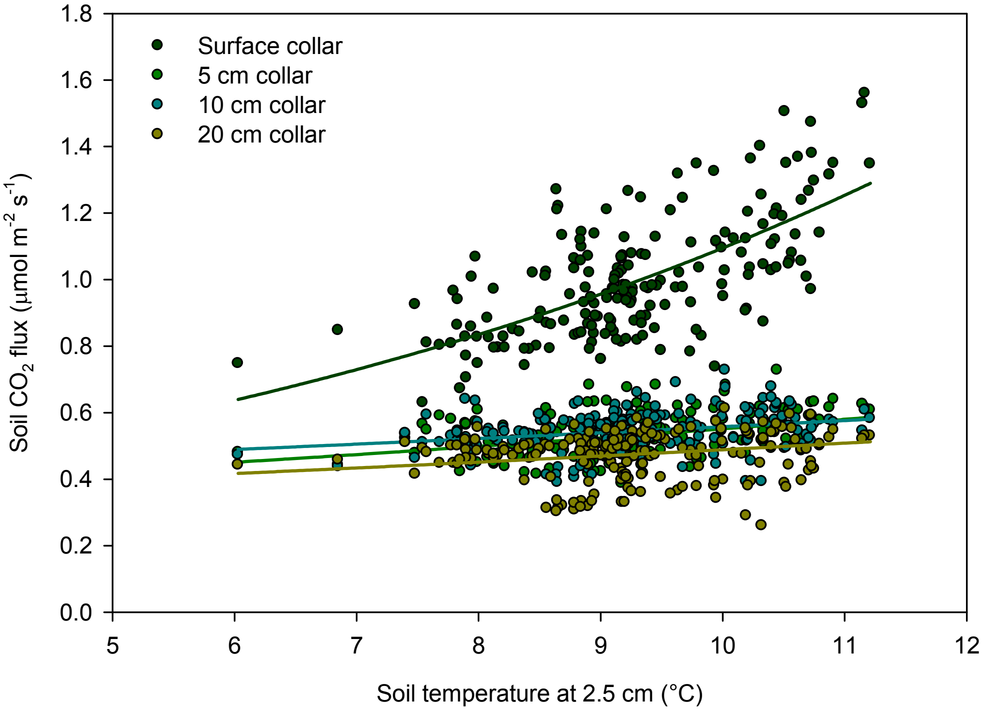


Figure 4-5: Hourly soil CO_2 fluxes plotted against soil temperature for the post-treatment, continuous monitoring period (10 to 19 October 2006) for the four treatments (surface: $y = 0.28 *e(0.14x)$, $R^2 = 0.44$; 5 cm: $y = 0.33 *e(0.05x)$, $R^2 = 0.15$; 10 cm : $y = 0.40 *e(0.03x)$, $R^2 = 0.07$; and 20 cm collars: $y = 0.38 *e(0.02x)$, $R^2 = 0.01$).

Examination of the data for the period of continuous monitoring showed that for the majority of the time, fluxes were clearly higher from the surface collars than the fluxes from the three deeper collar treatments which were clustered together with overlapping error bars (Figure 4-4). Apparent exceptions to this occurred once on the 11 and 12 October and again on the 18 October; during these periods surface collar fluxes were again higher, but the magnitude of the fluxes from the other treatments separated out in order of collar depth: 5 cm > 10 cm > 20 cm. This pattern coincided with the only significant rainfall events during the post-treatment period and soil moisture data showed peaks in the near surface soil moisture content of the peat during and immediately following these events. To examine this further, the 'treatment effect' was calculated for each hourly data point as the difference between fluxes from the surface collars and each of the inserted collar treatments. Figure 4-6 shows the relationship between the calculated treatment effects and soil moisture status. There was a significant positive relationship, showing that there was a greater treatment effect when soil conditions were wetter. Further, there was evidence that this relationship was stronger under deeper collar treatments; R^2 value of 0.25 for the 5 cm collar treatment compared to 0.52 for the 20 cm treatment.

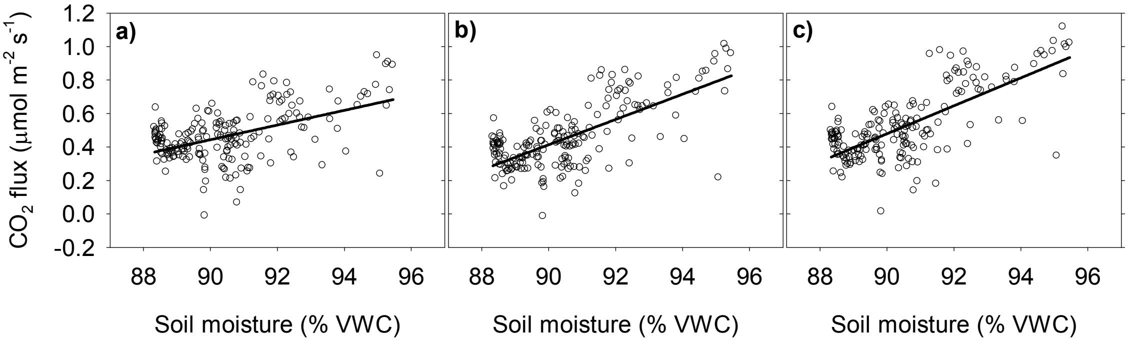


Figure 4-6: Relationships between the 'treatment effect' of collar insertion (surface collar flux – inserted collar flux) and soil moisture. a) 5 cm collar treatment effect ($y = 4.39x - 3.510$, $R^2 = 0.25$, $p < 0.0001$); b) 10 cm treatment effect ($y = 7.5469x - 6.3784$, $R^2 = 0.49$, $p < 0.0001$) and c) 20 cm treatment effect ($y = 8.3462x - 7.0323$, $R^2 = 0.52$, $p < 0.0001$).

4.3.3 Longer-term effects

Following the period of automated measurements, experimental plots were monitored using manual chamber surveys. These manual surveys showed that the collar depth treatment effect was a long-term effect, persistent after over twenty months. Generally, fluxes were highest from surface collars and decreased in the order 5 cm > 10 cm > 20 cm; however these differences were not always statistically significant and in those cases where differences were significant, they were between the surface collar and 20 cm collar treatments only (Section a) of Figure 4-7).

Collars were removed on 21 July 2008 to test the effect of removing the impediment to water drainage. This resulted in a dramatic change in the magnitude of the fluxes from the deepest collar treatment in particular; the 20 cm collar treatment switched from fluxes that were significantly lower than surface collars, to a situation where fluxes were significantly higher than from all other treatments (Section b) of Figure 4-7). Over the following week, plots were allowed to drain; after four days fluxes were not significantly different between treatments (25/07/08 - $p > 0.05$); after a further three days, fluxes were again significantly higher from surface collars than from the 20 cm collar treatment (28/07/08 - $p < 0.05$).

The final section of the graph in Figure 4-7, shows the effect of the final phase of the experiment; where the peat around all plots (in all treatments) was cut to a depth of 20 cm. Following this treatment of no differences in drainage and roots cut to an equal depth, soil CO_2 fluxes were similar across all ‘treatments’, with no significant differences (11/08/08 and 22/08/08 - $p > 0.05$).

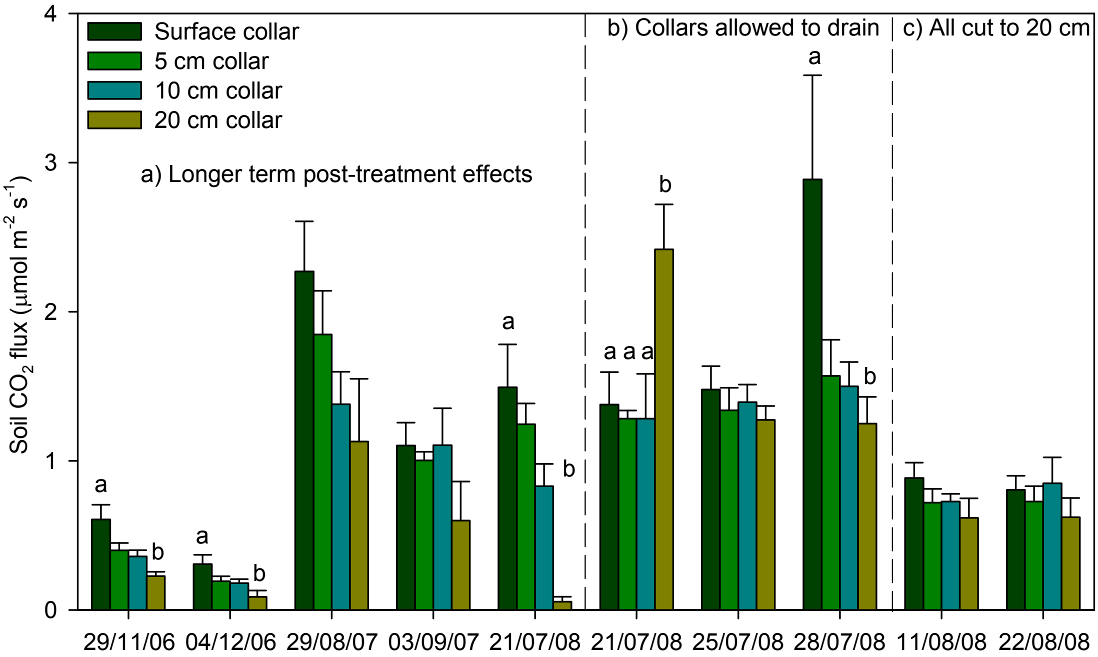


Figure 4-7: Following the period of continuous monitoring (Figure 4-2), soil CO_2 fluxes over the same plots were monitored at intervals during the subsequent 22 months using a manual survey chamber. Each bar represents the mean (*n* = 4) and error bars show + one standard error. For dates when treatments showed statistical significance, different letters (e.g. a or b) signify treatments that were significantly different from one another at the 0.05 level.

The graph shows samples taken during three distinct time periods: a) longer term collar depth treatment effects, up to 22 months after initial collar insertion; b) on 21/07/08 inserted collars were removed to allow water-logged soils to drain; and c) on 28/07/08 roots were cut to a depth of 20 cm around all plots but no collars were inserted.

Manual surveys of soil temperature and soil moisture within the collar plots aimed to identify whether collar insertion had an effect on the soil environment. Mean soil temperatures at 5 cm within the collars are shown in Table 4-1; there was no evidence of any significant soil temperature differences between treatments ($p > 0.05$). The results of a similar soil moisture survey (Table 4-2) showed relatively high soil moisture values at all times and across all treatments, which was consistent with data from the automated sensors (Chapter 3) which showed the peat to be close to saturation for much of the year. There is the suggestion of a treatment effect, with surface collars being consistently drier than the deeper collars, while the deepest collar treatment was always saturated. However, apart from the 20 cm treatment, the values were often highly variable within treatments, meaning that differences were not statistically significant ($p > 0.05$).

Table 4-1: Mean soil temperatures (°C) at 5 cm depth measured within collar plots for the four collar depth treatments (n = 4) ± one standard error. One-way ANOVA ($^{\#}$non-parametric alternative) statistics show that soil temperature did not differ significantly at the 0.05 level. Data were collected manually at intervals throughout the experiment.

Date	Surface collar	5 cm collar	10 cm collar	20 cm collar	F	d.f.	p
12/10/06	10.2 ± 0.1	10.1 ± 0.2	10.2 ± 0.1	9.9 ± 0.1	1.200	3	0.352
24/10/06	7.6 ± 0.1	7.5 ± 0.1	7.4 ± 0.1	7.3 ± 0.1	$6.843^{\#}$	3	0.077
06/11/06	6.8 ± 0.2	6.7 ± 0.1	6.7 ± 0.1	6.7 ± 0.1	0.488	3	0.697
14/11/06	5.4 ± 0.1	5.2 ± 0.1	5.1 ± 0.0	5.1 ± 0.1	$5.707^{\#}$	3	0.127
11/12/06	4.7 ± 0.1	4.2 ± 0.0	4.1 ± 0.1	4.4 ± 0.2	$7.697^{\#}$	3	0.053
29/08/07	11.4 ± 0.2	11.4 ± 0.2	11.4 ± 0.2	11.6 ±0.1	0.340	3	0.797
03/09/07	10.5 ± 0.2	10.7 ± 0.2	10.4 ± 0.1	10.7 ± 0.2	$1.474^{\#}$	3	0.688

Table 4-2: Mean soil volumetric water content (%) at 5 cm depth measured within collar plots for the four collar depth treatments (n = 4) ± one standard error. Kruskal-Wallis one-way ANOVA statistics show that soil moisture did not differ significantly at the 0.05 level. Data were collected manually at intervals throughout the experiment.

Date	Surface collar	5 cm collar	10 cm collar	20 cm collar	F	d.f.	p
12/10/06	74.2 ± 10.5	88.6 ± 7.0	87.7 ± 9.8	100.0 ± 0.0	5.455	3	0.141
24/10/06	80.6 ± 9.2	99.6 ± 0.4	89.5 ± 5.4	100.0 ± 0.0	7.420	3	0.060
30/11/06	89.7 ± 9.1	100.0 ± 0.0	97.0 ± 3.0	100.0 ± 0.0	4.177	3	0.243
06/11/06	76.4 ± 9.5	100.0 ± 0.0	92.7 ± 0.0	100.0 ± 0.0	7.624	3	0.054
14/11/06	92.9 ± 5.2	100.0 ± 0.0	97.6 ± 2.4	100.0 ± 0.0	7.015	3	0.071
11/12/06	94.8 ± 5.2	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0	3.000	3	0.392
29/08/07	88.4 ± 6.0	98.5 ± 1.5	97.0 ± 2.1	100.0 ± 0.0	5.512	3	0.138
03/09/07	93.8 ± 6.2	100.0 ± 0.0	99.8 ± 0.2	100.0 ± 0.0	2.150	3	0.542

4.3.4 Root distribution

Exploratory soil pits showed that there was very little live root material below a depth of 20 cm, so the root distribution within top 20 cm of peat was studied in detail (Table 4-3). The majority of the live roots, both in terms of length and mass (65 % and 69 % respectively) were located within the 5 cm below the surface. There was significantly less live root material in the 5 – 10 cm peat layer ($p < 0.05$) than the top layer. The 10 - 20 cm layer had significantly less root material ($p < 0.05$) with only ~3 % of the total root length and mass of the whole core found within this deepest layer of peat.

Table 4-3: Total root length (cm cm^{-3}), total root mass (mg cm^{-3}) and average root diameter (mm) ± one standard error, obtained from sample cores ($n = 3$) taken from close to the experimental plots in November 2006. Superscript letters show significant differences of variables between peat depth layers at the $p < 0.05$ level (One-way ANOVA with LSD post-hoc test).

Peat depth (cm)	Root length (cm cm^{-3})	Root mass (mg cm^{-3})	Root diameter (mm)
0 – 5	28.24 ± 3.80 ^{a}	4.64 ± 0.85 ^{a}	0.65 ± 0.01
5 – 10	13.94 ± 1.91 ^{b}	1.86 ± 0.21 ^{b}	0.48 ± 0.01
10 – 20	0.59 ± 0.13 ^{c}	0.10 ± 0.04 ^{c}	0.38 ± 0.01

The data presented in Table 4-3 were used to estimate the amount of live roots that would have been severed as a result of inserting measurement collars to the treatment depths of 0 cm, 5 cm, 10 cm and 20 cm. Further, the cumulative lost flux was calculated for each of the treatment depths, this was defined as the difference between the mean total flux (surface collars) and the mean fluxes measured with each of the inserted collars for the period 11 – 19 October 2006. The amount of root material 'excluded' by the inserted collars and the calculated lost flux followed a similar and near exponential increase with increasing peat depth (Figure 4-8). Both the majority of roots cut and the majority of the calculated lost flux occurred within the uppermost 5 cm; after this point, both variables begin to level off with increasing peat depth.

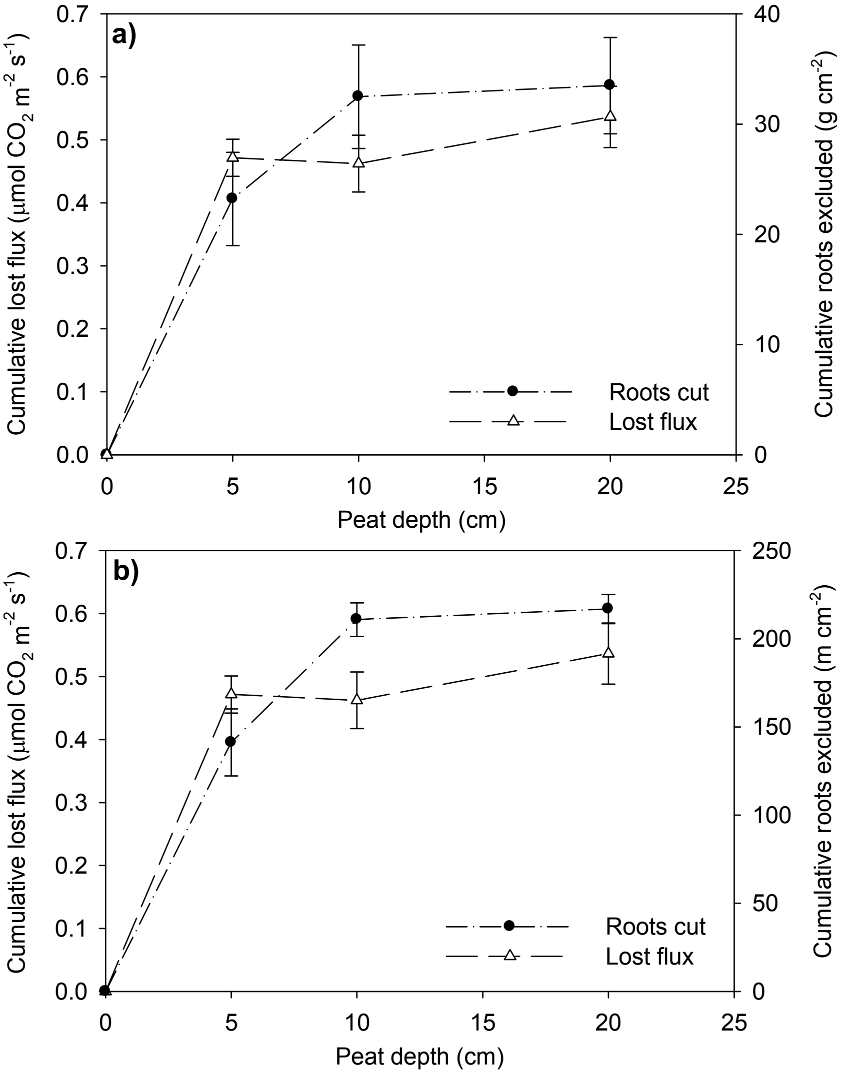


Figure 4-8: Relationships between peat depth and the cumulative roots excluded (filled circles: a) root mass; b) root length) and the calculated lost flux (open triangles). Points are means (*n* = 3 for root data and *n* = 9 for lost flux data), bars show ± one standard error.

4.4 Discussion

The common practice of inserting collars into the soil in order to take chamber measurements of soil CO_2 fluxes was found to have a significant effect on the magnitude of the measured fluxes. Collars were inserted on the 09 October 2006 and high temporal resolution measurements identified that within 24 hours, fluxes were significantly lower from treatments where collars had been inserted into the peat. During the following ten days, mean daily fluxes were around 50 % lower from the inserted collar treatments and as much as 65 % lower from the deepest collar treatment. This effect was found with collar depths (5 cm, 10 cm and 20 cm) that are frequently used in soil CO_2 flux studies in the published literature e.g. 10 - 15 cm (Blodau *et al.*, 2007; Glatzel *et al.*, 2003); 20 cm (Ward *et al.*, 2007); 15-30 cm (Strack & Waddington, 2007).

A search of the literature suggests that there is only one other study which has addressed similar issues and that was in a very different ecosystem, a larch forest in China. Wang *et al.* (2005) conducted a collar depth experiment, with collar insertion treatments varying between 0.3 cm and 8 cm. They found the soil CO_2 flux to be 40 - 50 % lower when measured with the deeper collars (5 and 8 cm) compared to the flux measured with 0.3 cm collars. In common with this study, they found a positive relationship between collar depth and the amount of roots severed by collar insertion. Their study provided a snapshot of the situation, being based on just a single set of measurements at one point in time. Nevertheless, these findings compare favourably with the results presented in this chapter in a quite different ecosystem. Wang *et al.* (2005) found no differences in temperature or soil moisture between treatments and they concluded that the effect was due to root cutting caused by collar insertion. While not studying the effects of collar insertion directly, Silvola *et al.* (1996) report the results of the only study to quantify the autotrophic component of soil CO_2 fluxes in peatland soils. They isolated peat columns by cutting to a depth of 40 - 50 cm and inserting plastic sheeting to prevent root regrowth. Across a number of different peatland types in Finland, fluxes were between 10 % and 45 % lower from root exclusion plots compared to controls. This difference was attributed to the root-derived component of respiration; supporting this, they found that the greatest differences occurred in peatlands with high proportions of vascular, rooting vegetation and the lowest from bogs dominated by *Sphagnum* spp.

The authors do not report any soil moisture or water table effects of their plastic sheeting treatment, so it is assumed that this was not a factor in their study. Buchmann (2000) used inserted collars to partition fine root respiration from heterotrophic soil respiration. This was achieved by comparing soil CO_2 fluxes from established collars to those from collars inserted 24 hours prior to measurement, with the former representing a trenching treatment (heterotrophic respiration) and the later representing total soil CO_2 flux. However, as both treatments involved cutting roots to a depth of 5 - 8 cm, it seems likely that the control or 'total soil CO_2 flux' will have suffered some reduction in the autotrophic component. The data presented in this chapter showed a collar insertion effect after less than 24 hours. This seems to cast some doubt on Buchmann (2000)'s estimates of 70 % heterotrophic respiration versus 30 % fine root respiration; if their 'control' had already been subject to a reduced flux, then the true autotrophic component would be greater than the 30 % they calculated. This would fit with the average 50:50 ratio in temperate coniferous forest soils reported in a recent metaanalysis (Subke *et al.*, 2006).

A detailed investigation into root distribution at the site (Table 4-3) provided evidence that inserting collars even to a depth of just 5 cm would have severed a significant number of roots. Separating this root material from the living plants would halt the process of respiration in those roots and act to stem the supply of photosynthates from the live plants to soil microbes. Experiments which have aimed to sever the supply of carbon to the roots and soils by clipping above ground vegetation or tree-girdling have demonstrated rapid declines in soil CO_2 fluxes within days in grasslands (Wan & Luo, 2003) and a month in a Scots pine forest (Högberg *et al.*, 2001). It can be envisaged that severing the roots themselves and imposing a barrier could explain the extremely fast response of fluxes to collar insertion in this study.

Measurements taken over the following 22 months (Figure 4-7) showed that the longer-term treatment effect was less significant, especially for the intermediate collar depth treatments (5 and 10 cm). One possibility is that over this medium-term time period, roots grew to recolonise the peat within the collars and this is sometimes used to justify inserted collars by stating that collars were inserted several months before measurements commenced in order to minimise disturbance and allow root regrowth. However, it seems unlikely that roots would grow up to recolonise the plots and

Buchmann (2000) found no evidence of live roots having grown into the collars from below after seven months. Another possible explanation is increased heterotrophic respiration from inserted collar treatments due to the decomposition of the recently severed roots. This is known to be in an issue with trenching experiments, which has been ignored by many studies (Subke *et al.*, 2006), but been shown to be a significant soil CO_2 source in others (Ngao *et al.*, 2007). Ngao *et al.* (2007) estimated that decomposing roots as a result of severing in a trenching experiment, accounted for up to 54 % of the total annual CO_2 flux in two temperate broadleaved forests.

There was evidence that the situation was more complex than a simple root-cutting effect in this study. The high temporal resolution data available for the days after collar insertion, suggested that at times there was a link between the pattern of fluxes and the soil moisture status of the peat. Immediately following rainfall episodes, fluxes from surface collars remained higher, but uniquely for the measurement period, there were treatment differences between the three inserted collar treatments, in order of insertion depth: 5 cm > 10 cm > 20 cm. Automated sensors showed that the soil moisture of the peat peaked during these periods and it was hypothesised that heavy rainfall results in temporary uneven drainage of plots with collar depth. At times deep collars extend down below the water table, after heavy rainfall the peat can become saturated, but deep collars prevent lateral flow. Under these circumstances, the peat within deeper collar treatments became wetter and at times water pooled above the surface. Although a number of manual soil moisture surveys of the peat within the collars were unable to identify significant differences, this may have been because significant differences were transient and dependent on rainfall during the preceding hours. Also, it seems likely that the manual soil moisture sensors were unable to resolve differences when the peat approached saturation; for example, wet peat and peat with surface water are visibly different and likely differ in respiratory processes but both recorded a soil moisture status of 100 % volumetric water content. However, it was possible to identify a relationship between the ‘treatment effect’ (i.e. the difference between surface collar fluxes and inserted collar fluxes) and the soil moisture of the peat at the automated sensors. As the peat became wetter, inserted collar treatments had increasingly lower fluxes compared to surface collars. Furthermore this relationship was stronger for the deeper collar treatments. This provides evidence that at some times and to some degree, the differences observed between the fluxes from the collar depth treatments was a result of inserted collars affecting the soil moisture status of the plots. While attempts to establish relationships between soil CO_2 fluxes and naturally occurring fluctuations in soil moisture and water table depth in peatlands have been mixed (Ise *et al.*, 2008; Lafleur *et al.*, 2005); experimental manipulations generally show that raising the water table results in a decline in soil CO_2 fluxes (Blodau *et al.*, 2004; Freeman *et al.*, 1993; Moore & Knowles, 1989).

Experiments towards the end of the monitoring period showed the impact of collars on soil CO_2 fluxes by changing the hydrology within the plots. When inserted collars were removed on 21 August 2008 there was a large pulse of CO_2 released from the deepest collar treatments, measured two hours afterwards. After collars were removed, excess water could drain from the deeper collar treatments, such that all treatments were subject to similar hydrological conditions. After a week (28 August 2008), the pulse of CO_2 from the 20 cm treatment had subsided and the relative fluxes had returned to the earlier pattern of significantly greater fluxes from the surface collar treatment compared to the 20 cm collar treatment. Having removed the cause of the unequal hydrology, it is suggested that the difference that remained was due to a long-term and persistent root-cutting effect in the 20 cm collar treatment. A final test added weight to this theory, the peat around all collars was cut to a depth of 20 cm, essentially simulating a 20 cm inserted collar but without the drainage issues. Two surveys over the following three weeks showed that the significant difference evident on 28 August was no longer present.

The temperature response of the soil CO_2 flux differed between treatments. Soil temperature explained much more of the variation in fluxes from the surface collar treatments compared to the inserted collar treatments. The calculated Q_{10} was also greater for the surface collars compared to the 5 cm treatment (3.62 compared to 1.63). The data has suggested two mechanisms by which collar insertion has affected the measured fluxes, root-cutting and altered soil moisture status. Can these two mechanisms explain the observed different temperature sensitivities? Firstly, root-cutting will mean that to some degree, the treatments are measuring fluxes from different sources. While surface collars measure the total soil CO_2 flux, inserted collars will exclude a proportion of the autotrophic root-derived flux and be more influenced by the heterotrophic component. There is mixed evidence for the two components exhibiting different temperature sensitivities. Schindlbacher *et al.* (2008) reported separate Q_{10} values that were not significantly different in a coniferous forest, while Boone *et al.* (1998) found the autotrophic component to be significantly more temperature sensitive in a mixed temperate forest. The results from this study are consistent with the later theory of greater temperature sensitivity from the autotrophic component of the soil CO_2 flux. Secondly, there is the potential role of soil moisture; higher soil moisture levels at certain times, may have acted to dampen the overall response to temperature. Illeris *et al.* (2004) found that soil moisture status moderated the temperature sensitivity of CO_2 exchange in a subarctic heath. Either mechanism described above, or more likely, a combination of the two, could have resulted in the observed differing temperature sensitivities.

4.4.1 Partitioning the soil CO_2 flux

Originally, it was hoped that this potential problem with measuring soil CO_2 fluxes could be turned into an advantage; by excluding the autotrophic component of soil respiration, the experimental manipulation of collar insertion could be seen as analogous to 'trenching' experiments. This technique, commonly applied in forest systems aims to partition the soil CO_2 fluxes into its heterotrophic and autotrophic components (Hanson *et al.*, 2000; Högberg *et al.*, 2009; Jassal & Black, 2006). However, it seems likely that the unique hydrology of peatlands contributed towards a more complex situation, whereby collar insertion had a duel effect on soil CO_2 fluxes. Collar insertion will reduce the measured flux due to partial severing of the autotrophic component of respiration. In addition to this effect, collars were found to affect the soil moisture of the peat, by impeding lateral flow of rainwater. The evidence is that this results in a systematic error in the measured fluxes, as the magnitude of the effect will vary with the soil moisture status of the peat. In generally wet conditions, impeded drainage will be a significant problem within inserted collars; while after a dry spell, the water table will drop and the peat within all collars will have the opportunity to 'dry out'. In this experiment, it was not possible to adequately tease apart the relative contribution of these two effects on the measured soil CO_2 flux. An experimental design to resolve this issue would involve a series of treatments similar to this experiment, but with additional 'collars' which would act to sever and impede root growth but would not alter the soil moisture/water table position of the plot. A design utilising a fine mesh similar to that employed by Heinemeyer *et al.* (2007) to determine the contribution of ectomycorrhizal fungi to forest soil CO_2 efflux, would likely prove fruitful.

4.4.2 Implications

In addition to the undesirable situation in which we might be underestimating the magnitude and importance of the soil CO_2 flux at studied sites, there is the danger of these measurement errors being incorporated into process-based models. For example, a key parameter in many land-surface or soil-vegetation-atmosphere models, is the temperature sensitivity of soil respiration, or Q_{10} (Cox, 2001; Cox *et al.*, 2000; Sitch *et al.*, 2003). Estimates of the Q_{10} parameter, whether it be for specific sites or for regional or global model runs are largely derived from chamber-based soil CO_2 flux studies. Qi *et al.* (2002) showed that relatively small variations in Q_{10} could be responsible for large and significant changes in model predictions of regional carbon balances; Schimel *et al.*'s (2000) estimate of the conterminous USA being a carbon sink could switch to a source if the uncertainty of soil respiration temperature sensitivity is considered. This study suggested that by altering the soil environment, using CO_2 flux data from collars inserted into the soil can affect our estimates of the true sensitivity of soil respiration to temperature.

Chamber-based soil CO_2 fluxes are often relied upon to test or validate estimates of ecosystem respiration derived from the eddy covariance method (Loescher *et al.*, 2006). Clearly, it is vital that potential errors and uncertainties behind chamber-based data are minimised in order to reduce the likelihood that these errors are fed into important studies concerning the carbon balance of ecosystems and their responses to environmental change.

4.4.3 Recommendations

This study has provided evidence that inserting collars to depths commonly seen in other studies can significantly reduce the measured soil CO_2 flux. It is believed that these findings justify the decision to employ surface collars which will reduce the effect of an important source of error associated with chamber-based measurements of soil CO_2 fluxes. This improved methodology was used to collect the soil CO_2 flux data which contributes to the following chapter. The findings emphasise that great care and consideration should be employed when measuring soil CO_2 fluxes with chamber-based methods. Conventional technology dictated that deep, inserted collars were essential; it is recommended that in the absence of the equipment available to this study, researchers will have to develop innovative solutions that allow defensible chamber measurements without significantly altering the soil environment.

CHAPTER 5

CHAMBER MEASUREMENTS OF THE SOIL CO_2 FLUX

5.1 Introduction

5.1.1 Scope

The flux of CO_2 from soils to the atmosphere is a major component of the global carbon cycle, at an estimated 68 ± 4 Pg C yr^{-1} (Raich & Schlesinger, 1992). For comparison, burning fossil fuels is now estimated to contribute about 7.8 Pg yr^{-1} (IPCC, 2001). At individual ecosystem levels too, the soil CO_2 flux is important, often comprising the second largest carbon flux after gross primary productivity (GPP). The relationships between the different fluxes and the terms used in this chapter are summarised below. The net ecosystem exchange of CO_2 (NEE) is, at its simplest, the balance of the CO_2 uptake by GPP and CO_2 respired as ecosystem respiration (ER):

$$\mathrm{NEE} = \mathrm{GPP} - \mathrm{ER} \tag{5.1}$$

ER is itself the sum of several processes. Often, for practical purposes it is defined as the sum of above-ground plant respiration (R_a) and soil respiration (R_s):

$$\mathrm{ER} = \mathrm{R_a} + \mathrm{R_s} \tag{5.2}$$

However, soil respiration is the product of fluxes from several different organism types and is often defined as:

$$\mathrm{R_s} = \mathrm{R_{sa}} + \mathrm{R_{sh}} \tag{5.3}$$

where R_{sa} is autotrophic soil respiration and R_{sh} is heterotrophic respiration. So the following equation represents a more complete description of the gaseous CO_2 fluxes in terrestrial ecosystems:

$$\mathrm{NEE} = \mathrm{GPP} - \mathrm{R_a} - \mathrm{R_{sa}} - \mathrm{R_{sh}} \tag{5.4}$$

In forest ecosystems R_s as a whole can typically contribute 30 – 80 % of ER depending on the season or 63 % of GPP (Curtis *et al.*, 2005; Davidson *et al.*, 2006). Many of the studies which have looked at the contribution of R_s relative to the whole system carbon balance have taken place in forests, where the focus has been on determining the role that R_s plays in countering the carbon sequestration benefits of photosynthesis and assimilation (Heath *et al.*, 2005). Estimates of the annual budgets of soil CO_2 fluxes are not particularly abundant for peatlands. In recent years, there has been a far greater focus on using eddy covariance technology to measure the net fluxes of CO_2 between the land surface and atmosphere (Aurela *et al.*, 2002; Humphreys *et al.*, 2006; Lafleur *et al.*, 2001; Lafleur *et al.*, 2003; Lloyd, 2006). While these studies are useful for determining whether an area is a net sink or source of CO_2, the figures generated are the sum of the whole range of processes described above with carbon moving in different directions. A more complete understanding of the mechanisms and their vulnerability to change will come from detailed studies of the individual pathways. For example, just as R_s is an important control on the carbon balance in forests, so it is important in controlling the large carbon stores in organic soils. When peatlands are sinks of carbon, it is usually because the unique conditions suppress the decomposition of organic matter, which is a large component of the R_s flux (Blodau, 2002; Charman, 2002). Understanding the factors which affect the magnitude of the R_s flux is therefore vital for understanding and predicting changes to the overall carbon balance of these important ecosystems.

The differences between the terms ‘soil respiration’ and ‘soil CO_2 flux’ were set out in Chapter 4 and as such, the measurements described throughout this chapter are again referred to as soil CO_2 fluxes. Even at single sites, soil CO_2 fluxes can show large spatial and temporal variations (Buchmann, 2000). Spatial variation may be due to variations in a range of complex factors: vegetation type, root nitrogen concentrations, soil texture, substrate quantity and quality and soil moisture (Boone *et al.*, 1998; Buchmann, 2000; Davidson *et al.*, 2006; Rayment & Jarvis, 2000; Xu & Qi, 2001). Soil CO_2 fluxes also exhibit temporal variation at a range of timescales, with the controlling variables differing considerably depending on the type of ecosystem. A diurnal cycle driven by soil temperature is often obvious (Rayment & Jarvis, 2000; Xu & Qi, 2001), but correlations have also been found with photosynthesis, suggesting a controlling role for short-term substrate supply (Davidson & Janssens, 2006; Liu *et al.*, 2006; Tang *et al.*, 2005). Longer-term variations are largely driven by some combination of temperature and soil moisture, with the relative roles being highly variable. Where water is unlikely to be a limiting factor, the fluxes will usually follow seasonal trends of soil temperature or radiation (Davidson *et al.*, 2006); whereas in more arid ecosystems, soil CO_2 flux may follow the soil moisture dynamics (Davidson *et al.*, 2000). In northern peatlands, soil temperature is important, but there is no consensus regarding soil moisture or water table depth. Some studies have found no effect of these latter factors (Lafleur *et al.*, 2005; Parmentier *et al.*), while others have (Moore & Dalva, 1993; Moore & Knowles, 1989; Silvola *et al.*, 1996). The reality is that it is likely highly dependent upon the hydrology of individual sites.

5.1.2 Aims

Chapter 3 considered the net gaseous CO_2 fluxes at the site and Chapter 4 provided evidence of the importance of carefully considering how to measure fluxes using the chamber technique. This fifth chapter builds on those findings by using the improved methodology to make high temporal resolution measurements of soil CO_2 fluxes over a seven month period. These data are used to present an estimate of the annual soil CO_2 flux for the site. Specifically, the following questions are addressed:

- What is the spatial variation of soil CO_2 fluxes at the site? And how much of the observed variation is spatially-dependent?

- Does vegetation type affect the magnitude of the soil CO_2 flux significantly?

- Does the time of measurement significantly affect estimates of total CO_2 fluxes?

- What environmental variables drive soil CO_2 fluxes and are they different for different times of the year?

- And finally, what is the net flux of carbon from the soils to the atmosphere during the seven month period and for an annual period?

5.2 Methods

5.2.1 Field site

The experiment was conducted at the Bog End area of the Moor House reserve (54° 41’ 27” N, 02° 21’ 50” W; 564 m elevation). The site is described in detail in Section 2.4 and measurement plots were established 5 m to the south-west of the eddy covariance flux tower described in Chapter 3.

5.2.2 Chamber CO_2 measurements

Soil CO_2 fluxes were measured using a LI-8100 closed dynamic chamber system (LI-COR, Lincoln, Nebraska, USA). The system could either be used with the IRGA and a single survey chamber (Model 8100-103) to make manual measurements or attached to nine long-term chambers (Model 8100-101) for continuous monitoring via a custom built multiplexer unit (Electronics Workshop, Biology Department, University of York, UK). Both chamber designs had a 20 cm diameter with chamber volumes of 4.84 L (survey chamber), 4.09 L (long-term chambers) and a flow rate of 1.5 L min^{-1}. Collars of 20 cm diameter and constructed from PVC drain pipe material were installed at each plot. In all cases, surface collars were used; these extended 10 cm above the surface, but did not cut into the peat. During measurements, chambers were placed over the collars, with a rubber gasket maintaining the seal (Figure 5-1). The CO_2 flux was calculated as the linear increase in CO_2 concentration based on one second measurements during a chamber closure period of 1 – 2 minutes (Heinemeyer *et al.*, 2006). The measurements from the initial 20 s form a ‘dead band’, while steady mixing is achieved within the system, and were not used to calculate fluxes.

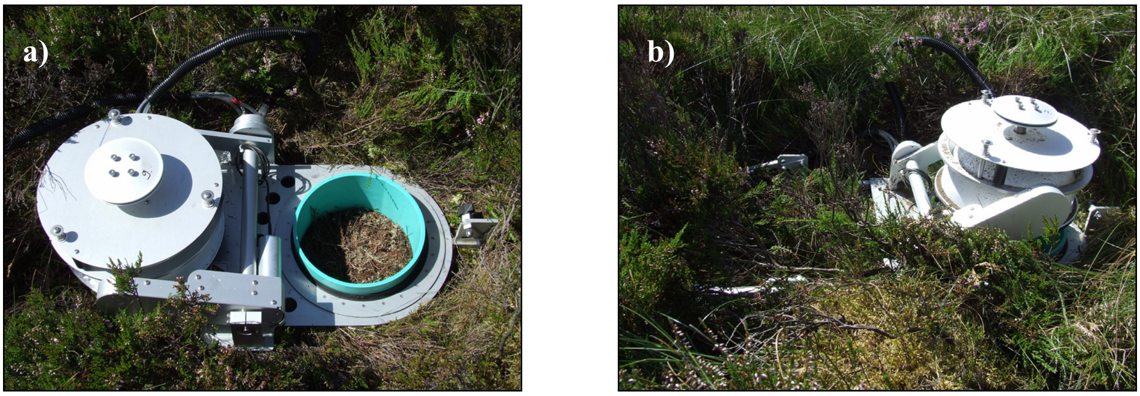


Figure 5-1: Photographs of the LI-8100 long-term automated soil CO_2 flux chambers in position at Bog End, Moor House; a) chamber in the open position and showing a measurement collar around a 20 cm diameter plot; b) chamber approaching the closed position.

5.2.3 Experimental design

The Calluneto-Eriophoretum plant community is dominated by *Calluna vulgaris*, *Eriophorum vaginatum* and 'Moss spp.' and at a landscape scale is remarkably homogeneous, being composed of relatively evenly spaced but distinct 'patches' of these three vegetation types. Three 4 m^2 blocks were randomly designated within a 100 m^2 area to the south-west of the eddy covariance flux tower. Within each block, plots were identified in each of the three vegetation types, such that there were nine plots in total with three replicates of each vegetation type. As in Chapter 4, the aim was to measure the soil CO_2 flux rather than ecosystem respiration, meaning that there should be no live above-ground vegetation within collars. This was achieved by placing collars in naturally occurring gaps in *Calluna* and *Eriophorum* patches; in 'Moss spp.' patches, live, green vegetation was removed by clipping at the beginning and throughout the experiment.

Collars and long-term chambers were installed on 26 July 2006, with measurements beginning the following day. With the exception of a three week break in October 2006, when the system was deployed to monitor the collar depth experiment (Chapter 4) and some shorter gaps due to equipment failure, hourly measurements continued up until 05 March 2007.

5.2.4 Ancillary measurements

The experimental site was within 5 m of the eddy covariance flux tower, so the full range of climate and environmental measurements described in Chapter 3 were available to this study. Briefly, these included, air temperature, relative humidity, wind speed and direction, net radiation, photosynthetically active radiation, soil temperature and soil moisture. Precipitation and solar radiation data were again available from the ECN weather station, approximately 750 m from the study site.

5.2.5 Vegetation survey

In August 2008, a simple vegetation survey was carried out within the flux footprint area in order to scale the chamber measurements at the patch scale to be more representative of the landscape. Six 30 m long transect lines were established within an area of landscape surrounding the eddy covariance flux tower (approximate diameter of 300 m). At 0.5 m intervals, the vegetation in a 20 cm diameter patch was classified as *Calluna, Eriophorum,* 'Moss spp.' or 'other'.

5.2.6 Surveying spatial variation of soil CO_2 fluxes

The spatial variation of soil CO_2 fluxes was examined using data collected during three measurement campaigns along a transect which ran from south-west to north-east through the typical flux footprint area. On 26 June 2006 measurements were taken along a 115 m stretch of the transect, following the recommendation that the lag distance should be no more than one third of the total transect length, this allowed an estimation of the variation along 35 m sections at a scale of 5 m. On 26 July 2006 measurements were taken along a 168 m section, allowing estimates of the variation along 50 m sections at a scale of 5 m. To assess variation at a finer scale, measurements were made every metre along a 30 m transect on 31 August 2007. In addition to this, for the first 7.5 m, measurements were made every 0.25 m., this design allowed an estimation of the variation along: a) 2.5 m sections at a scale of 0.25 m, and b) 10 m sections at a scale of 1 m.

Geostatistics were used to evaluate the degree of spatial autocorrelation among measurement points; these were performed with the GS+ package (Geostatistics for the

Environmental Sciences, v. 9.0, Gamma Design Software, Plainwell, MI). The semivariance $\gamma(h)$ is estimated using the following equation:

$$\gamma(h) = \frac{1}{2n(h)}\sum_{x=1}^{n}(z_x - z_{x+h})^2 \tag{5.5}$$

where $n(h)$ is the number of lag pairs at distance intervals of h, whilst z_x and z_{x+h} are the measured sample values at location x and $x + h$. The semivariance is calculated for all possible pairs of points in the data set, with each pair being assigned to a distance interval class h. The semivariance expresses the degree of the relationship between two points along the transect and can be plotted against distance to inform about the spatial pattern of a property, such as soil CO_2 flux (e.g. Figure 5-2). Analyses usually involve fitting a model to the data, in order to estimate the key parameters of the relationship: the intercept on the y-axis (the *nugget*, C_0), equal to the variation that is random and not spatially correlated; where a property shows spatial dependence, the semivariance will increase with distance over the *range* (a), until it levels out at a level known as the *sill* (C_0+C_1). The sill is equal to the overall variance of the series, the range is the distance within which sample points are spatially-dependent (Burrough, 1995).

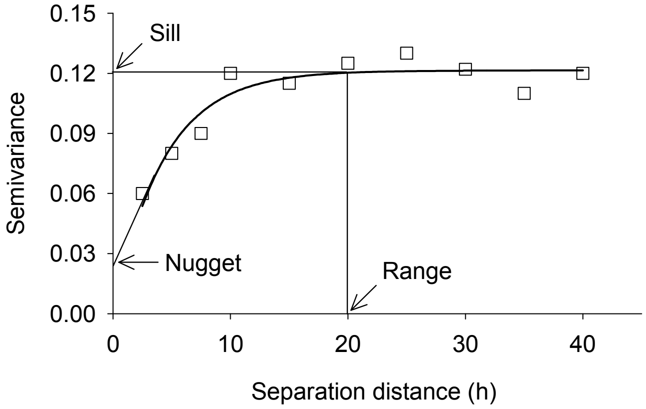


Figure 5-2: An example semivariogram with data points and a fitted model showing the key parameters.

5.2.7 Time of measurement effects

The availability of high temporal resolution, hourly flux measurements allowed an investigation into the effect of the time of measurements on the magnitude of fluxes. In experiments where manual chambers are used, flux measurements will usually be made during the hours around midday e.g. Ward *et al.* (2007). To simulate the effect of taking such measurements and simply interpolating them to the rest of the day, 'peak day' daily fluxes (13:00) and 'middle day' daily fluxes (11:00 – 15:00) were created and these were compared to the 'true' daily fluxes of measurements from a full 24 hours.

5.2.8 Soil CO$_2$ flux models

Three commonly used models were used to describe the response of soil CO$_2$ fluxes (SF) to temperature T. Each model includes a number of parameters which were fitted by minimising the root mean square error (RMSE) using the Solver function in Microsoft Office Excel 2007 (Microsoft Corporation, Redmond, Washington, USA).

1. The exponential model (van't Hoff, 1884):

$$\mathrm{SF} = R_b e^{\beta T} \qquad \textbf{(5.6)}$$

where, R_b and β are both fitted parameters > 0.

2. The Arrhenius (1898) equation:

$$\mathrm{SF} = R_{10} e^{E_0 T^{-1}} \qquad \textbf{(5.7)}$$

where, of the two fitted parameters, $R_{10} > 0$ and $E_0 < 0$. E_0 is interpreted as the activation energy, expressed using the temperature scale and temperature is measured in Kelvin.

3. The Lloyd & Taylor (1994) model. This is a modified Arrhenius model with the addition of a third parameter T_0:

$$\mathrm{SF} = R_{10} e^{E_0 (T_0 + T)^{-1}} \qquad \textbf{(5.8)}$$

where, of the three fitted parameters, $R_{10} > 0$, $E_0 < 0$ and $T_0 < 273.15$.

The temperature sensitivity of the soil CO_2 flux is assessed by the Q_{10} factor. This is the factor by which respiration is multiplied when temperature increases by 10 º and can be calculated with the following equation:

$$Q_{10} = e^{\beta \times 10} \qquad \textbf{(5.9)}$$

where β is determined by fitting equation 5.2 to the data.

5.2.9 Statistical analysis

For the period of continuous monitoring, mean daily CO_2 fluxes were calculated for the three vegetation types and were compared by using one-way repeated measures analysis of variance (ANOVA) with between-subjects comparisons. Data were log transformed for normality prior to analyses. Non-parametric Kruskal-Wallis tests were used to test if soil temperature and moisture levels differed between vegetation plots during manual surveys. The Regression Wizard in SigmaPlot 10 (Systat Software, Inc., Chicago, Illinois, USA) was used for regression analysis to determine relationships between environmental variables, fluxes and model residuals and for assessing model fit by plotting measured versus modelled fluxes. One-way repeated measures ANOVAs with between-subjects comparisons were applied to monthly datasets in order to test whether flux time of measurement affected the daily flux totals. Finally, standard multiple regressions were used to incorporate temperature and soil moisture as independent variables in a model to describe the variation in summer soil CO_2 fluxes.

Unless otherwise stated, statistical analyses were performed using SPSS version 12.0.1 (SPSS Inc, Chicago, Illinois, USA).

5.3 Results

5.3.1 Vegetation survey

The vegetation at Bog End is dominated by the Calluneto-Eriophoretum plant community. The percentage cover of the three main vegetation types within the landscape was estimated based on the results of a vegetation survey carried out in August 2008 (Table 5-1). *Calluna* was the most dominant vegetation type (56.8 ± 2.8 %) followed by *Eriophorum* (33.6 ± 3.3 %) and 'Moss spp.' (22.9 ± 2.2). The survey allowed for the classification of a point as 'other', but no points were encountered where the dominant vegetation was anything other than the three main types.

Table 5-1: Percentage cover of the three main vegetation types which dominate the Calluneto-Eriophoretum plant community of the blanket bog at Bog End, Moor House NNR.

Vegetation classification	Percentage cover	Standard error
Calluna	56.8	2.8
Eriophorum	30.6	1.6
Moss spp.	12.6	1.8
Other	0.0	0.0

5.3.2 Spatial variation of soil CO_2 fluxes

Soil CO_2 flux data were collected at points along a transect within the typical Calluneto-Eriophoretum plant community on three days during three summer months (26 June 2006, 26 July 2006 and 31 August 2007). Data were collected primarily for the purposes of assessing the spatial variation in soil CO_2 fluxes, rather than temporal changes. Summary statistics are shown in Table 5-2; the surveys showed that fluxes were highly variable along the transect, with relatively high coefficients of variation (CV) of between 37 and 54 %. On a single day in August 2007, for example, fluxes varied from being negligible at 0.06 μmol m^{-2} s^{-1} at one location to relatively high soil CO_2 fluxes for a peatland of 3.53 μmol m^{-2} s^{-1}.

Table 5-2: Soil CO_2 fluxes (µmol m^{-2} s^{-1}) at Bog End, Moor House NNR. Measurements were taken along a 170 m transect. Abbreviations: SD = standard deviation; SE = standard error of the mean; *n* = number of measurements; and CV = coefficient of variation (as a percentage).

Date	Mean	SD	SE	Range	*n*	CV (%)
June 2006	2.18	0.82	0.16	1.25 – 4.62	27	37.45
July 2006	2.84	1.41	0.26	0.40 – 6.35	30	49.75
August 2007	1.63	0.89	0.11	0.06 – 3.53	61	54.43

The data presented in Table 5-2 show that soil CO_2 fluxes could be highly variable; geostatistics were then used to determine the degree to which this variation was spatially-dependent. A typical semivariogram showing a degree of spatially-dependent variation is shown in Figure 5-2. Semivariances are lowest between points that are closest together, showing that neighbouring points are more likely to share similar properties than points which are further apart. A distance is reached at which variation ceases to be spatially-dependent and the semivariance becomes equal to the random variation of the sample.

Distances between sampling locations along the transect in June and July 2006 allowed for an assessment of spatial variation at a minimum scale of 5 m. At the spatial scales sampled, there was no evidence of the variation in soil CO_2 fluxes being spatially-dependent. The nugget variance was equal to the sill variance and linear models approximating to the sample variance were fitted to the data. In general, fluxes from plots that were closer together were not more similar than those from plots that were further apart (Figures 5-3 and 5-4). In August 2007, measurements were taken from plots that were closer together (0.25 m) allowing an assessment of finer scale variation. Semivariograms produced for sampling at a 0.25 m scale (Figure 5-5) and a 1 m scale (Figure 5-6) again failed to show evidence of a spatial component to the measured variation in the soil CO_2 fluxes.

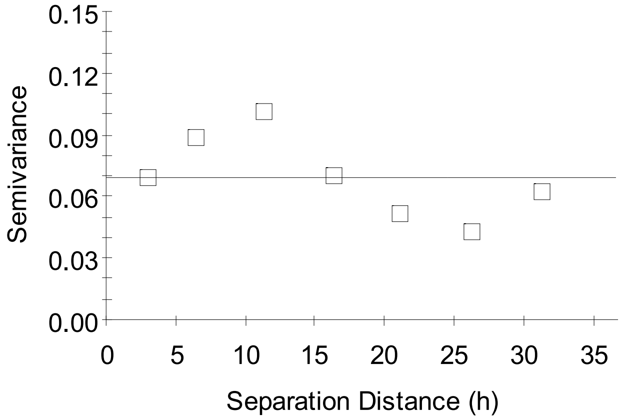


Figure 5-3: Semivariogram describing the spatial variation in soil CO_2 fluxes at a sampling scale of 5 m in June 2006, where the separation distance (h) is measured in meters.

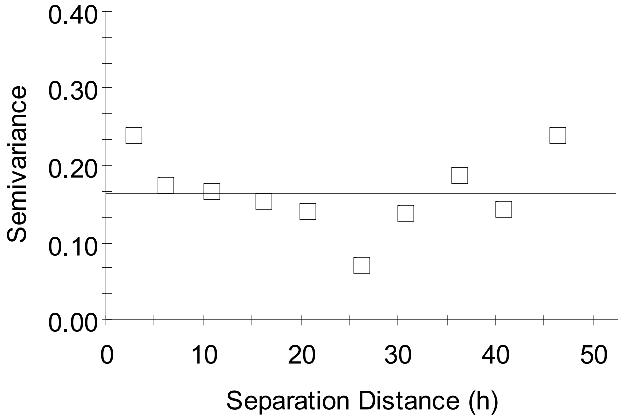


Figure 5-4: Semivariogram describing the spatial variation in soil CO_2 fluxes at a sampling scale of 5 m in July 2006, where the separation distance (h) is measured in meters.

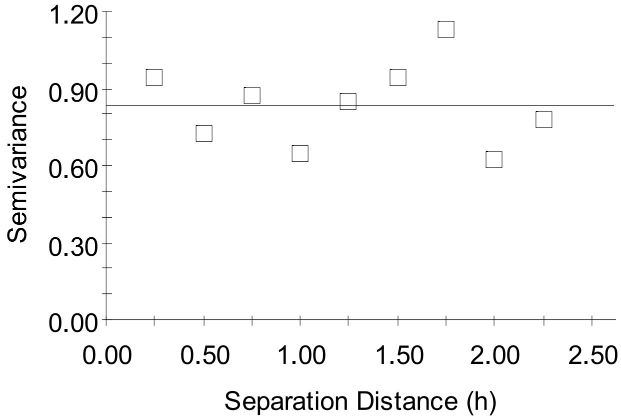


Figure 5-5: Semivariogram describing the spatial variation in soil CO_2 fluxes at a fine sampling scale of 0.25 m in August 2007, where the separation distance (h) is measured in meters.

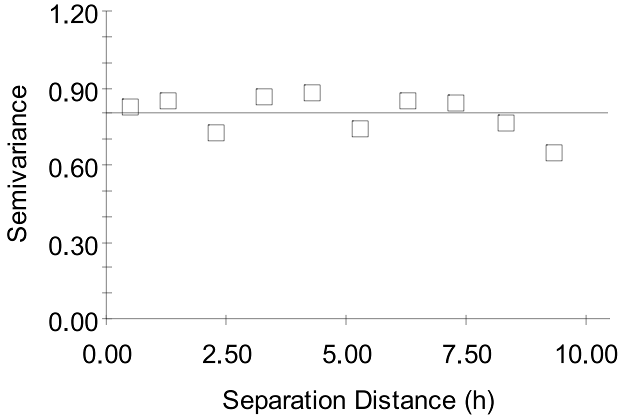


Figure 5-6: Semivariogram describing the spatial variation in soil CO_2 fluxes at a sampling scale of 1 m in August 2007, where the separation distance (h) is measured in meters.

5.3.3 Temporal variation of soil CO_2 fluxes

Soil CO_2 fluxes were measured hourly from July 2006 to March 2007. Peak hourly fluxes of 4.75 µmol m^{-2} s^{-1} were measured during the warm days towards the end of July 2006. Fluxes then gradually decreased over the end of the summer and into autumn, by December hourly fluxes were generally between 0 and 0.5 µmol m^{-2} s^{-1}. Nevertheless, mean hourly fluxes were positive throughout the winter, for example, the coldest air temperature recorded was -9.11 ºC at 06:00 on 25 December 2006 when a small positive flux of 0.10 µmol m^{-2} s^{-1} was measured.

5.3.4 Soil CO_2 flux and vegetation type

Long-term soil CO_2 flux chambers were placed within one of the three distinct vegetation type patches and daily means were calculated for the soil CO_2 fluxes from the vegetation patches (Figure 5-7). In general, mean daily fluxes were higher from the *Calluna* and *Eriophorum* patches than from the Moss patches.

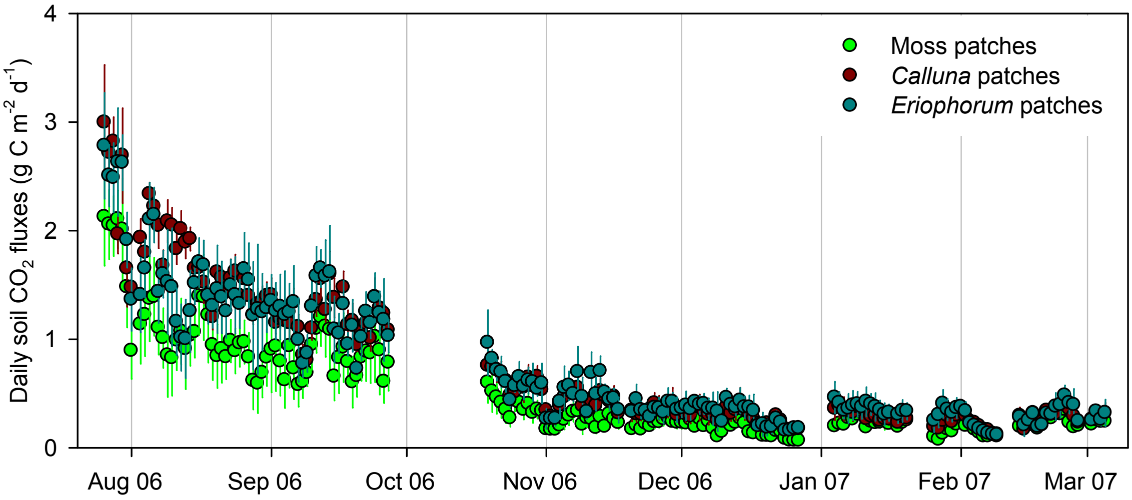


Figure 5-7: Daily soil CO_2 fluxes (g C m^{-2} d^{-1}) measured using chambers within each of three vegetation type patches. Points are means (n = 3) of daily totals ± one standard error.

The effects of time and vegetation type on daily soil CO_2 fluxes (g C m^{-2} d^{-1}) were examined using a one-way repeated measures ANOVA with between-subjects comparisons. The analysis showed that for all three time periods, the soil CO_2 flux changed significantly with time ($p < 0.005$) (Table 5-3). However, there was no evidence that the surrounding vegetation type had any significant effect on the overall mean of soil CO_2 fluxes, *p* values were greater than 0.05 for both the time × vegetation interaction term and the between-subjects (vegetation) test in all cases. An examination of the raw data identified one Moss plot as having consistently low fluxes, which were largely responsible for the low mean values observed in Figure 5-7, fluxes from the other Moss patches behaved similarly to those from the other vegetation types.

Table 5-3: Results a one-way repeated measures ANOVA with between-subjects comparisons testing the effects of time and vegetation type on the variation of daily soil CO_2 fluxes ($g\ C\ m^{-2}\ d^{-1}$).

Source of variation	*F*	d.f.	*p*
Period 1 – July to Sept 2006 (58 days)			
Within-subjects			
Time	7.80	2.30	0.004
Time × Vegetation	0.45	4.60	0.796
Between-subjects			
Vegetation	1.16	2.00	0.355
Period 2 – Oct to Dec 2006 (55 days)			
Within-subjects			
Time	10.04	2.30	0.001
Time × Vegetation	0.63	5.20	0.684
Between-subjects			
Vegetation	0.80	2.00	0.491
Period 3 – Dec to March 2007 (20 days)			
Within-subjects			
Time	16.43	2.29	0.0001
Time × Vegetation	1.26	4.58	0.336
Between-subjects			
Vegetation	1.20	2.00	0.364

Manual measurements of soil temperature within the soil CO_2 measurement collars were taken at intervals throughout the experiment period (Table 5-4). There were no consistent patterns and Kruskal-Wallis tests showed that there were no significant differences in soil temperatures between the three vegetation types ($p > 0.05$).

Table 5-4: Mean soil temperatures (°C) at 5 cm depth measured within collar plots for the three vegetation types (*n* = 3) ± one standard error. Kruskal-Wallis one-way ANOVA statistics show that soil temperature did not differ significantly at the 0.05 level.

Date	*Calluna*	*Eriophorum*	Moss	*F*	d.f.	*p*
27/07/06	11.93 ± 0.22	12.00 ± 0.10	12.07 ± 0.38	0.230	2	0.988
03/08/06	11.20 ± 0.15	11.03 ± 0.15	11.20 ± 0.17	0.836	2	0.658
30/10/06	9.43 ± 0.12	9.57 ± 0.09	9.70 ± 0.15	1.831	2	0.400
06/11/06	6.97 ± 0.17	6.93 ± 0.30	6.83 ± 0.20	0.391	2	0.822
14/11/06	5.23 ± 0.03	5.10 ± 0.12	4.93 ± 0.03	4.281	2	0.118
11/12/06	4.63 ± 0.13	4.33 ± 0.09	4.30 ± 0.12	3.621	2	0.164
05/03/07	3.33 ± 0.15	3.37 ± 0.15	3.57 ± 0.22	0.713	2	0.700

In a similar manner, soil moisture status within each of the soil CO_2 collars was monitored to test for any differences between the different vegetation patches. Soil moisture levels were high for all measurement surveys which is consistent with longer-term continuous monitoring at the site (Table 5-5). There were no significant differences in mean soil moisture content for any of the six surveys ($p > 0.05$).

Table 5-5: Mean soil volumetric water content (%) at 5 cm depth measured within collar plots for the three vegetation types (*n* = 3) ± one standard error. Kruskal-Wallis one-way ANOVA statistics show that soil moisture did not differ significantly at the 0.05 level.

Date	*Calluna*	*Eriophorum*	Moss	*F*	d.f.	*p*
27/07/06	80.41 ± 13.98	70.53 ± 16.99	77.74 ± 22.26	0.170	2	0.919
30/10/06	98.41 ± 1.59	94.83 ± 5.17	86.18 ± 13.82	0.125	2	0.939
06/11/06	100.00 ± 0.00	99.83 ± 0.17	86.97 ± 13.03	1.167	2	0.558
14/11/06	100.00 ± 0.00	96.63 ± 2.88	100.00 ± 0.00	4.500	2	0.105
11/12/06	100.00 ± 0.00	100.00 ± 0.00	86.56 ± 13.44	2.000	2	0.368
05/03/07	100.00 ± 0.00	93.56 ± 6.44	100.00 ± 0.00	2.000	2	0.368

5.3.5 Soil CO_2 flux and driving environmental variables

Considering the evidence presented in Table 5-3 that there were no significant differences in the mean soil CO_2 fluxes between the different vegetation types, the data from all nine chambers were combined to form single mean hourly figures. These data were then used to calculate daily totals of CO_2 emitted. Complete data existed for 162 days out of a total of 222 days of the measurement period from July 2006 to March 2007. Based purely on the available data, an estimated 114.92 ± 13.38 g C m^{-2} were emitted from the peat as the soil CO_2 flux (Figure 5-8).

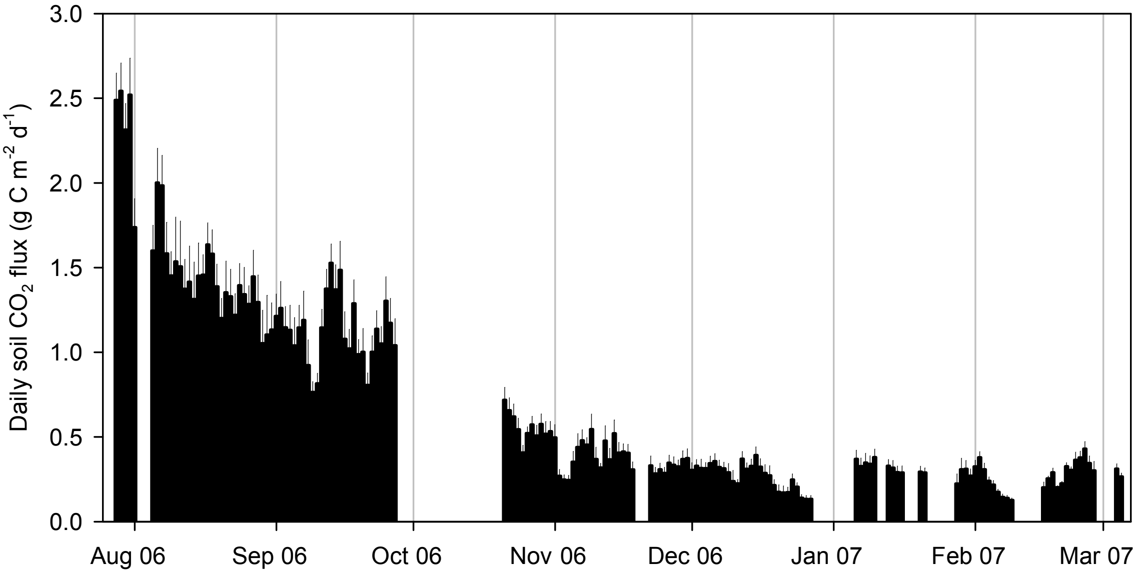


Figure 5-8: Daily soil CO_2 fluxes (g C m^{-2} d^{-1}), each bar is the mean of usually nine chambers for days when a full set of hourly measurements were available, fine error bars show + one standard error.

High temporal resolution, hourly data were used to explore relationships between soil CO_2 fluxes and driving environmental variables. The results of this exercise revealed improved understanding of the environmental controls on soil CO_2 fluxes and allowed the development of semi-empirical models to describe the fluxes during periods when measurements were not taken, to allow monthly, seasonal and annual flux totals to be estimated. The measurement period was divided into two parts; a summer period with relatively high soil CO_2 fluxes (July to September), and a winter period with relatively low measured fluxes (October to March).

Summer period

Temperature was an important factor in explaining the variation in summer soil CO_2 fluxes. The relationship could be described by a simple exponential model and this showed that soil temperature at 8 cm depth was a slightly stronger predictor of fluxes than was air temperature, with an R^2 value of 0.40 compared to 0.37. However, neither value was particularly high and so the fit of two other commonly applied models was also evaluated. Considering the relationship with air temperature first (Figure 5-9 & Table 5-6), neither the Arrhenius nor Lloyd & Taylor models provided a better fit to the data than the initial exponential model, which had the lowest root mean square error (RMSE) of 0.34 μmol m^{-2} s^{-1} and the best measured versus modelled data relationship (slope of fitted line = 0.41, intercept = 0.78). The same three models were applied to the soil temperature relationship (Figure 5-10 & Table 5-6). Over the range of temperatures observed, the three models behaved in a very similar manner, with neither of the additional models offering any improvement. The model fit statistics were similar, with the exponential model exhibiting slightly better performance, RMSE of 0.317 and a better measured versus modelled data relationship (slope of fitted line = 0.51, intercept = 0.65). The simple exponential model driven by soil temperature was therefore the preferred model of describing soil CO_2 fluxes during the summer period (Figure 5-11). However, there was a considerable degree of scatter around the relationship and the model seemed to perform particularly badly at representing the very high fluxes sometimes observed during warmer temperatures. Complete details of the parameters for all of the models are contained within Appendix 2.

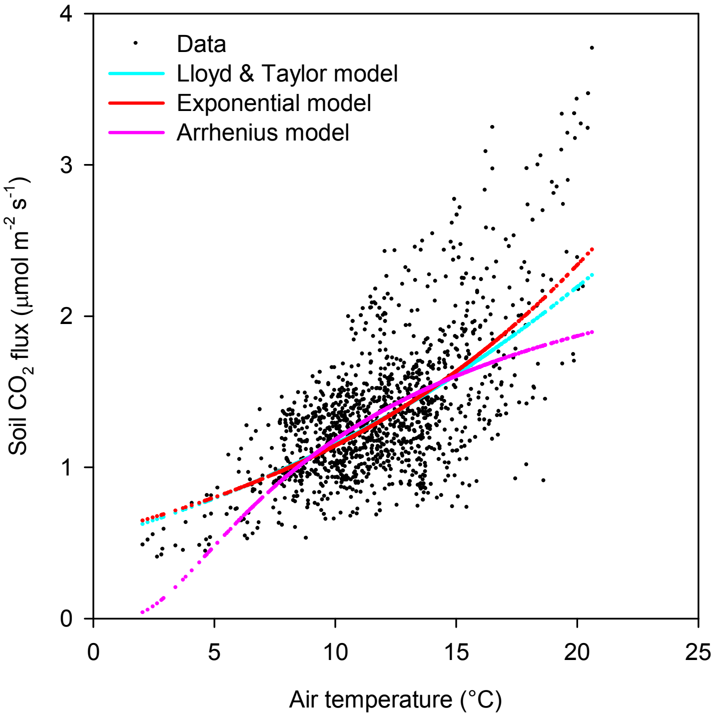


Figure 5-9: Relationship between soil CO_2 flux and air temperature during the summer period (July to September 2006).

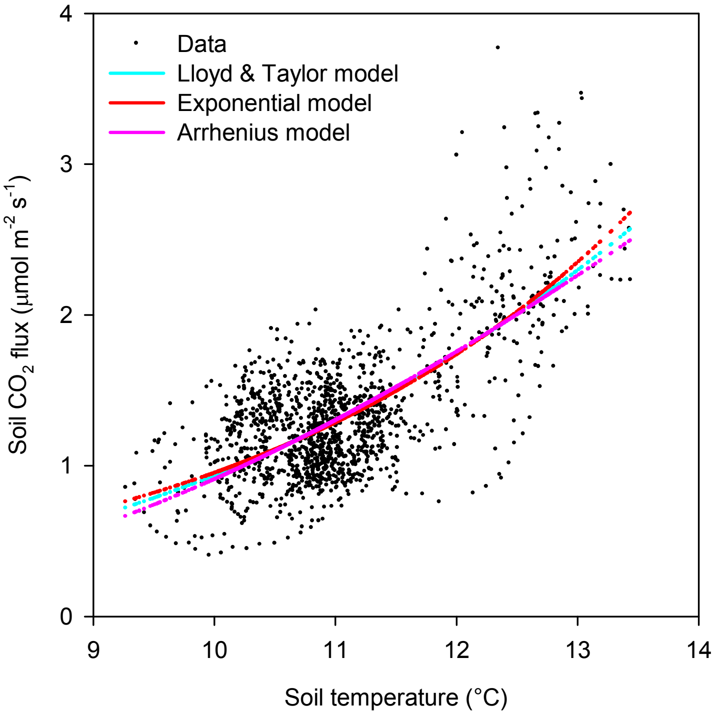


Figure 5-10: Relationship between soil CO_2 flux and soil temperature during the summer period (July to September 2006).

Table 5-6: Model performance statistics for three soil CO_2 flux models for the summer period (July 2006 to October 2006).

Temperature	Model	Measured *vs*. modelled	R^2	RMSE
Air	Exponential	$y = 0.415x + 0.775$	0.41	0.344
	Arrhenius	$y = 0.354x + 0.850$	0.34	0.365
	Lloyd & Taylor	$y = 0.372x + 0.833$	0.37	0.354
8.0 cm soil	Exponential	$y = 0.508x + 0.651$	0.50	0.317
	Arrhenius	$y = 0.495x + 0.667$	0.48	0.324
	Lloyd & Taylor	$y = 0.497x + 0.665$	0.47	0.320

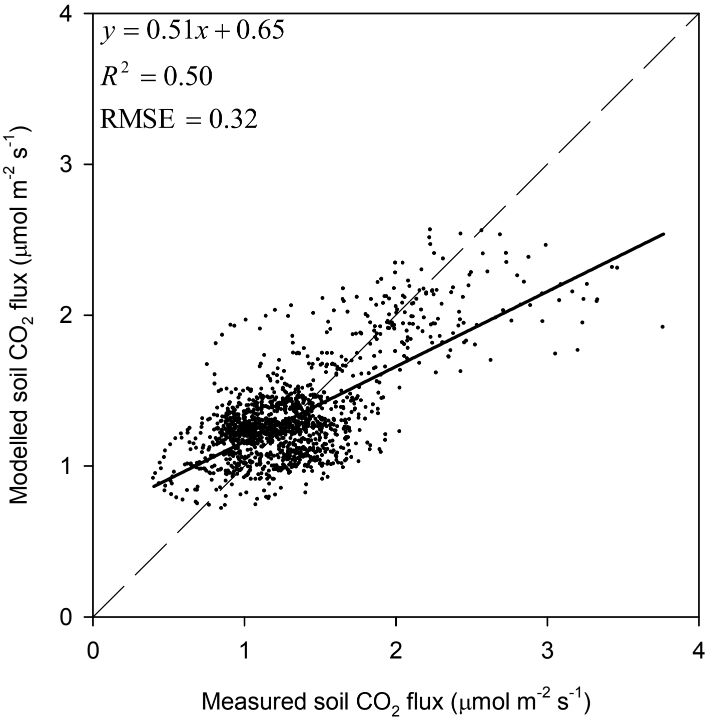


Figure 5-11: Modelled versus measured soil CO_2 fluxes for the summer period (July 2006 to September 2006). The exponential model driven by soil temperature measured at 8 cm provided the best fit to the data. Dotted line represents 1:1 relationship.

There was a negative relationship between soil moisture content and soil CO_2 fluxes. The highest fluxes were recorded when soil moisture was at its lowest level ($R^2 = 0.42$; $p < 0.0001$). Soil moisture levels were high for most of the summer period (in excess of 50 % volumetric water content (VWC)). The exception was a drought period in July when soil moisture dropped to around 40 % VWC (Figure 5-12). When these points were excluded from the regression analysis, soil moisture explained considerably less of the variation in soil CO_2 fluxes ($R^2 = 0.14$; $p < 0.0001$).

A common problem associated with determining the role of the environmental variables driving soil CO_2 fluxes is that soil temperature and soil moisture may co-vary with one another at certain times. To investigate whether soil moisture was related to soil CO_2 fluxes, independently of temperature, soil moisture was plotted against the residuals of the preferred temperature – soil CO_2 flux model (Figure 5-13). This showed a significant relationship; at low soil moisture levels, the temperature dependent model tended to under-predict fluxes; while at higher soil moisture levels, the model tended to over-predict the flux. The relationship remained significant even when the drought period data were excluded from the analysis ($y = 0.0106x - 0.818$; $R^2 = 0.20$; $p < 0.0001$).

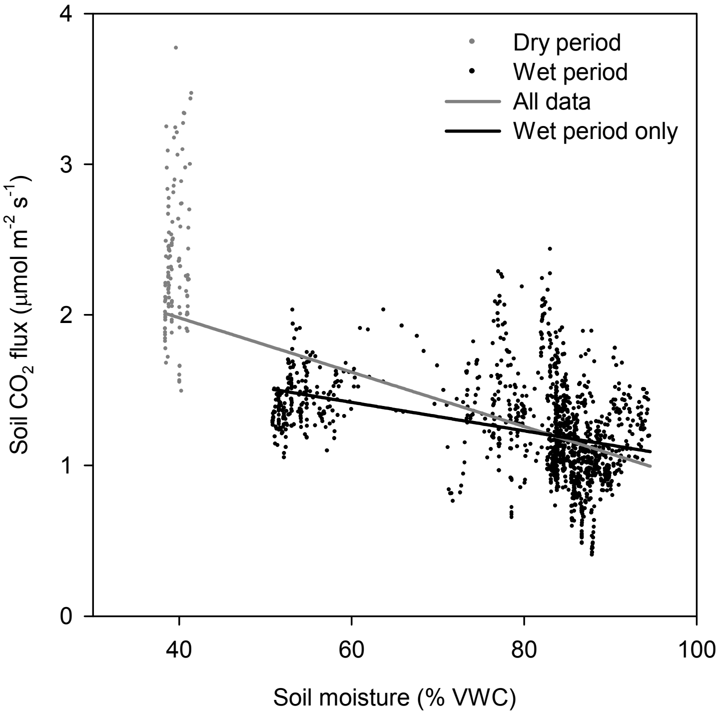


Figure 5-12: Relationship between soil CO_2 flux and soil moisture during the summer period (July to September 2006). The grey line shows the linear regression with all data ($y = -0.018x + 2.702$; $R^2 = 0.42$; $p < 0.0001$), the black line shows the relationship when data from a four day dry period in July are excluded ($y = -0.0094x + 1.986$; $R^2 = 0.14$; $p < 0.0001$).

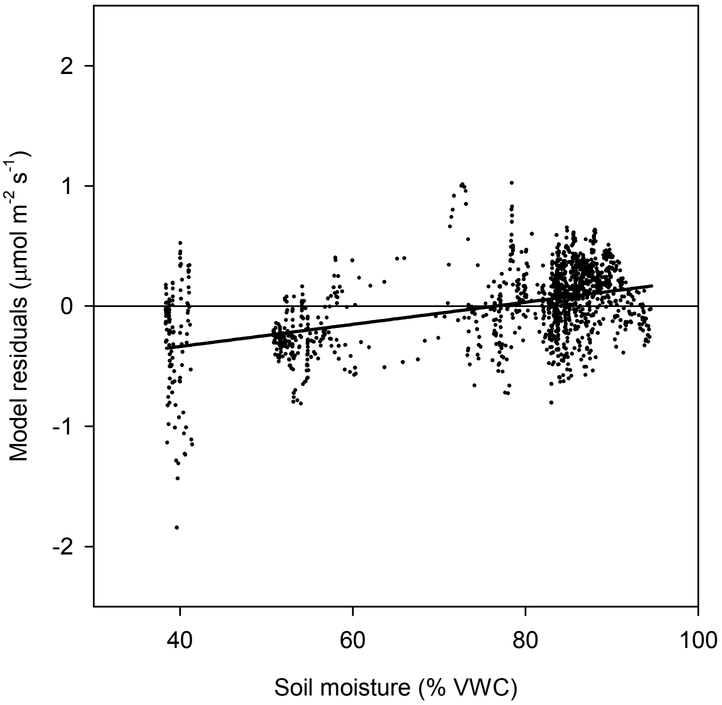


Figure 5-13: Relationship between soil moisture and the residuals of the temperature – soil CO_2 flux model ($y = 0.0092x – 0.705$; $R^2 = 0.21$; $p < 0.0001$).

In light of the evidence that both temperature and soil moisture were independently regulating soil CO_2 fluxes during the summer, multiple regression was used to explore these relationships and to combine the two independent variables into an improved model. A model combining soil temperature and soil moisture was able to explain 62 % (p <0.0005) of the variation in measured fluxes (Table 5-7). The analysis suggested that soil moisture (beta coefficient = -0.449; $p < 0.0005$) explained a similar amount of the variance as soil temperature (beta coefficient = 0.491; $p < 0.0005$).

An alternative model, using air rather than soil temperature, along with soil moisture, performed better, explaining 74 % (p <0.0005) of the variation (Table 5-7). This latter model suggested that soil moisture (beta coefficient = 0.615; $p < 0.0005$) made a larger contribution to explaining the variance than did temperature (beta coefficient = 0.563; $p < 0.0005$). This multiple regression model performed well compared to the models driven by temperature alone; the RMSE was 0.23 µmol m^{-2} s^{-1} and the measured versus modelled data relationship was improved considerably (slope of fitted line = 0.75, intercept = 0.33) (Figure 5-14). Complete details of the parameters for all models are contained within Appendix 2.

Table 5-7: Statistics from the two multiple regressions, combining air temperature and soil moisture (top panel) and soil temperature and soil moisture (lower panel).

	Coefficient	Standard error	*p*
Constant	1.618	0.040	< 0.0005
Air temperature	0.085	0.002	< 0.0005
Soil moisture	-1.709	0.038	< 0.0005
ANOVA: $F = 1984.78$; d.f. = 2; $p < 0.0005$; $R^2 = 0.74$			
Constant	-1.064	0.142	< 0.0005
Soil temperature	0.303	0.011	< 0.0005
Soil moisture	-1.247	0.050	< 0.0005
ANOVA: $F = 1161.75$; d.f. = 2; $p < 0.0005$; $R^2 = 0.62$			

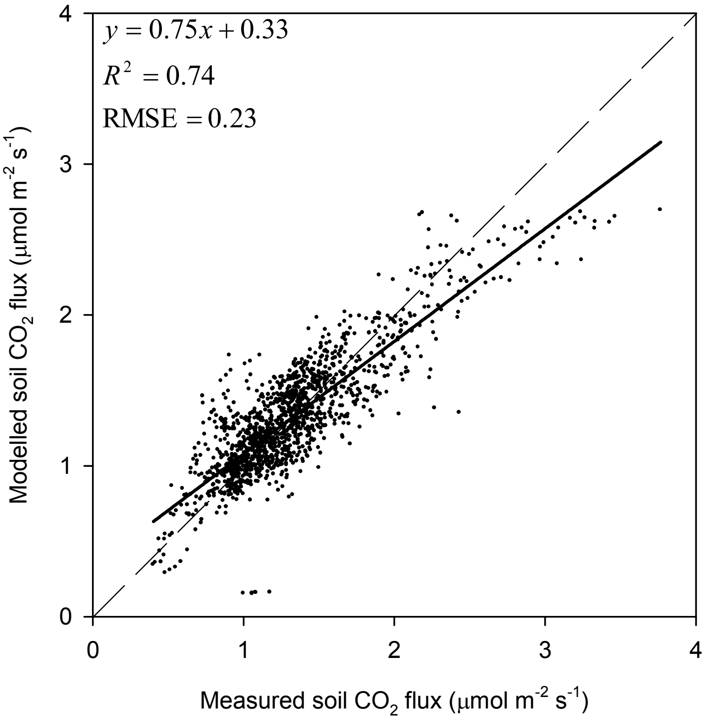


Figure 5-14: Hourly modelled versus measured soil CO_2 fluxes for the summer period (July 2006 to September 2006). The multiple regression model included both soil moisture and air temperature. Dotted line represents 1:1 relationship.

Winter period

During the winter period, temperature alone provided a better explanation of hourly soil CO_2 fluxes than during the summer period. The data closely fitted the simple exponential relationship driven by soil temperature at 2.5 cm depth (R^2 = 0.79) (Figure 5-15). Soil temperature at this depth yielded the better relationships than either air, canopy or deeper soil, temperatures (Table 5-8). The Arrhenius and Lloyd & Taylor models were applied to the data. The Arrhenius model again performed least well in terms of higher RMSE of 0.074 compared to 0.056 for both of the other models and the in terms of measured versus modelled data fit (slope of fitted line = 0.76, intercept = 0.071). The exponential and Lloyd & Taylor models again performed similarly well, with Lloyd & Taylor showing a marginally improved measured versus modelled data fit.

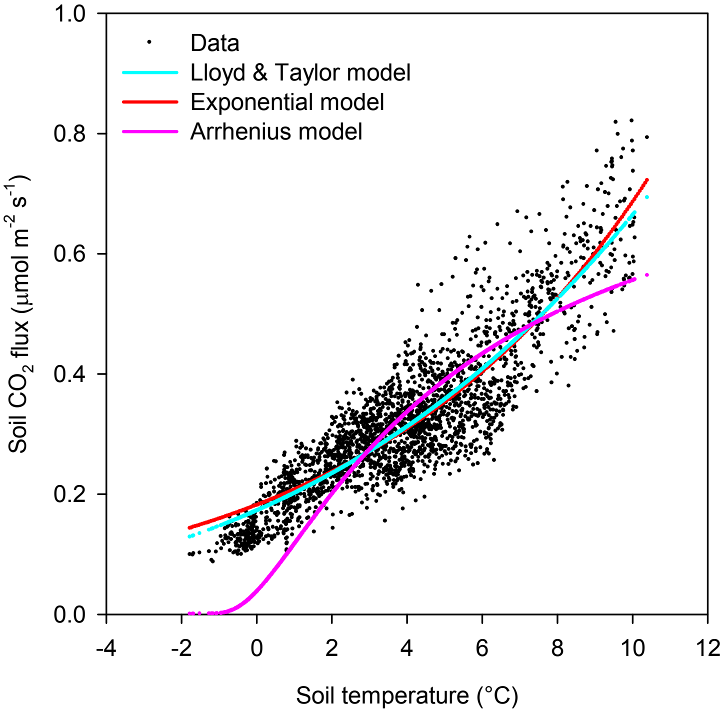


Figure 5-15: Relationship between soil CO_2 flux and soil temperature measured at 2.5 cm depth for the winter period (October 2006 to March 2007). Three models that are commonly used to describe the temperature response of soil respiration are fitted to the data.

Table 5-8: Model performance statistics for three soil CO_2 flux models for the winter period (October 2006 to March 2007).

Temperature	Model	Measured *vs*. modelled	R^2	RMSE
Air	Exponential	$y = 0.584x + 0.132$	0.58	0.080
	Arrhenius	$y = 0.599x + 0.106$	0.52	0.086
	Lloyd & Taylor	$y = 0.587x + 0.131$	0.58	0.080
Canopy	Exponential	$y = 0.647x + 0.112$	0.65	0.073
	Arrhenius	$y = 0.663x + 0.104$	0.60	0.079
	Lloyd & Taylor	$y = 0.650x +0.111$	0.65	0.074
2.5 cm soil	Exponential	$y = 0.785x + 0.069$	0.79	0.056
	Arrhenius	$y = 0.761x + 0.071$	0.71	0.074
	Lloyd & Taylor	$y = 0.793x + 0.066$	0.80	0.056
7.5 cm soil	Exponential	$y = 0.781x + 0.070$	0.79	0.057
	Arrhenius	$y = 0.781x - 0.063$	0.68	0.067
	Lloyd & Taylor	$y = 0.789x + 0.067$	0.79	0.056
8.0 cm soil	Exponential	$y = 0.707x + 0.094$	0.71	0.066
	Arrhenius	$y = 0.634x - 0.113$	0.60	0.078
	Lloyd & Taylor	$y = 0.709x + 0.093$	0.71	0.066
15 cm soil	Exponential	$y = 0.631x + 0.117$	0.63	0.075
	Arrhenius	$y = 0.590x - 0.129$	0.56	0.083
	Lloyd & Taylor	$y = 0.639x + 0.115$	0.63	0.075

The peat at Bog End was close to saturation point during the entire winter period, soil moisture was consistently above 90 % VWC. There was no relationship between soil moisture and soil CO_2 fluxes during this period (Figure 5-16; $p = 0.176$). This was confirmed by the lack of any pattern when the residuals of the preferred temperature model were plotted against soil moisture (Figure 5-17; $p = 0.955$). A model driven by temperature alone was deemed adequate to describe winter time soil CO_2 fluxes, the fit of the preferred Lloyd & Taylor model driven by 2.5 cm soil temperature is shown in Figure 5-18, complete details of the parameters for all models are contained within Appendix 2.

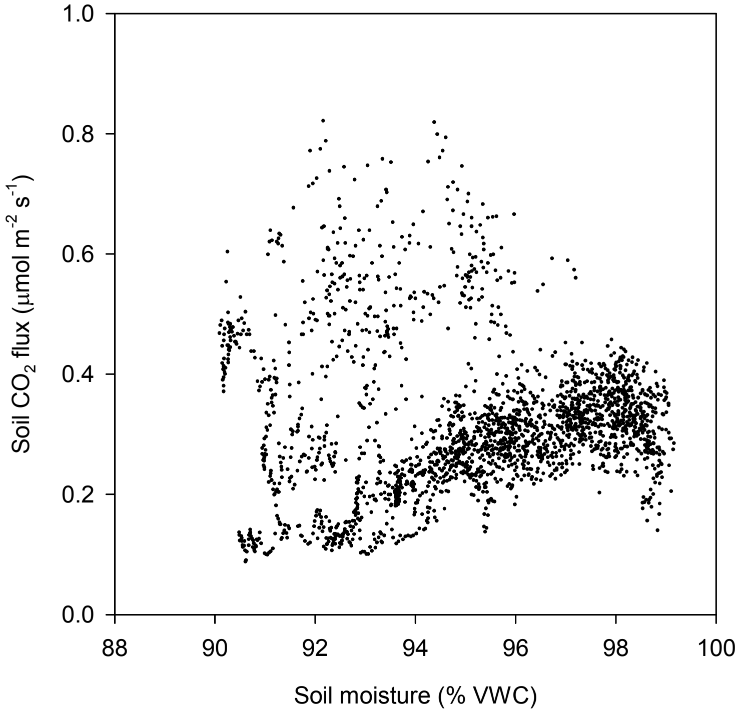


Figure 5-16: Hourly soil CO_2 fluxes plotted against soil moisture for the winter period (October 2006 to March 2007) ($y = 0.145x + 0.182$; $R^2 = 0.0008$; $p = 0.176$).

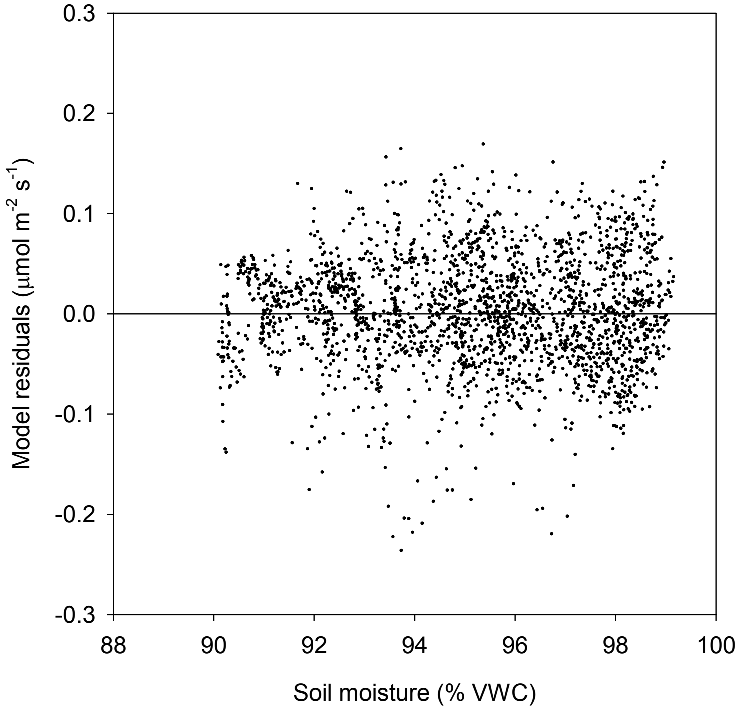


Figure 5-17: Plot of the temperature model residuals against soil moisture for the winter period ($y = 0.000027x – 0.0008$; $R^2 = 0.0000014$; $p = 0.955$).

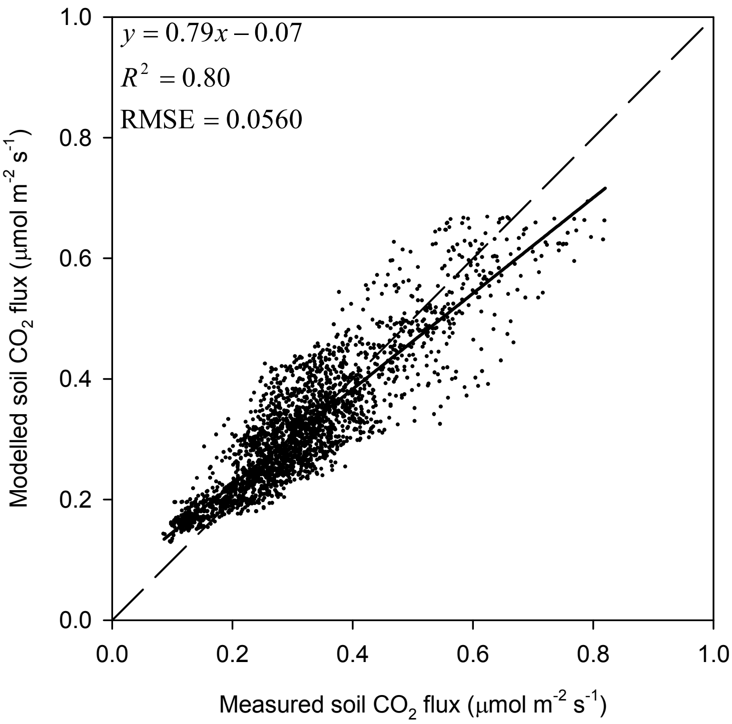


Figure 5-18: Hourly modelled versus measured soil CO$_2$ fluxes for the winter period (October 2006 to March 2007). The Lloyd & Taylor model driven by soil temperature measured at 2.5 cm provided the best fit to the data. Dotted line represents 1:1 relationship.

An examination of the data showed evidence of a strong diel cycle of soil CO$_2$ fluxes at certain times of the year; this was most pronounced during the growing season (July to October; Figure 5-19). During these months, fluxes peaked during a period between 13:00 and 16:00. In July, the lowest fluxes occurred during a night-time period between 22:00 and 04:00, by 05:00 fluxes began to rise towards their daily maximum. In August this rise began at around 07:00 and by September it was around 08:00. There was no evidence of such diel cycles during the winter months of November to February.

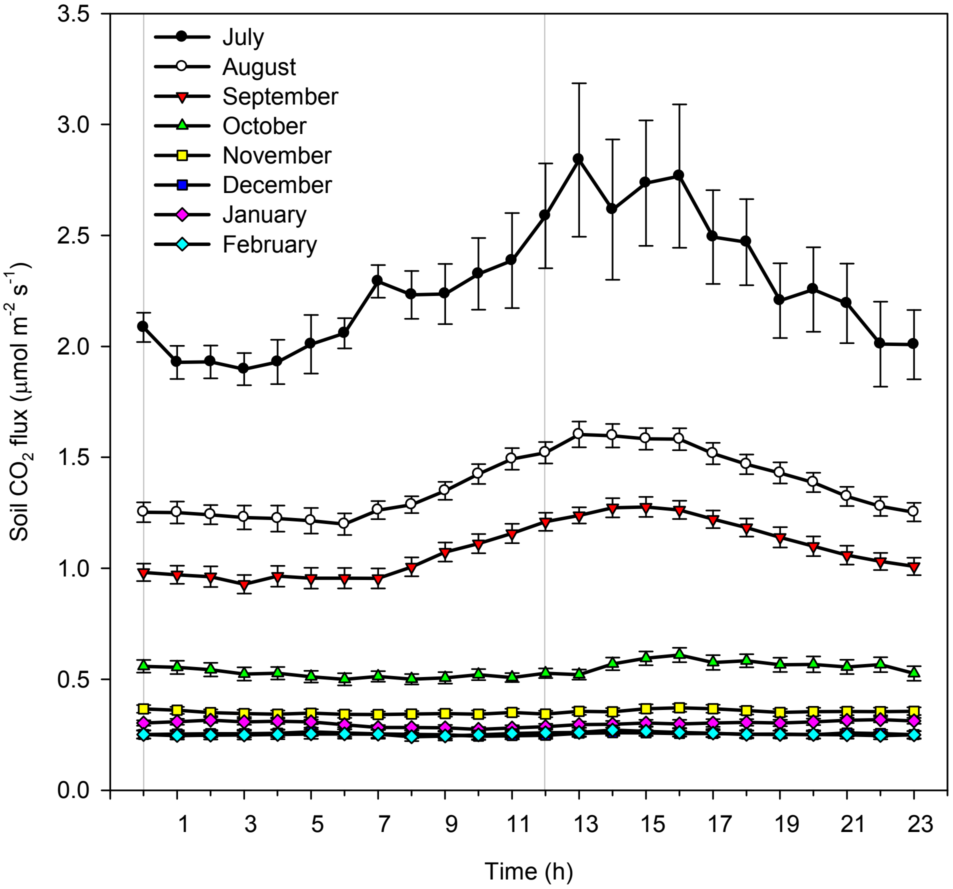


Figure 5-19: Monthly diel cycles of soil CO_2 fluxes. Data points are means of the available hourly data for each month, error bars are ± one standard error (July, *n* = 6; August, *n* = 31; September, *n* = 28; October, *n* = 14; November, *n* = 30, December, *n* = 27; January, *n* = 18; February, *n* = 22).

Figure 5-20 shows the daily cycles of air, canopy and soil temperatures measured at various depths averaged over the month of October 2006. The plot shows two important features, the first being the difference in amplitude of the diel cycles, with air and canopy temperatures unsurprisingly exhibiting the greatest variations and increasingly dampened responses with increasing depth of measurement. The second noteworthy point is the differences in phase of the diel cycles; while air temperature peaked at around noon, near-surface soil temperature (2.5 cm) peaked two hours later and 7.5 cm soil temperature peaked at around 15:00. Temperatures measured at greater depths lagged air temperature by as much as 12 hours. These differences in phase or lags are potentially important; one method to identify temperature-independent diel cycles relies on first establishing a relationship between fluxes and soil temperature (i.e. temperature-dependent fluxes) and then exploring potential cycles amongst the residuals (so-called temperature independent fluxes).

Figure 5-21 shows that the daily cycle of soil CO_2 flux in August tracks the daily cycle of air temperature much closer than soil temperature at 8 cm below the surface. The daily peak in soil temperature lags the peaks in air temperature and CO_2 fluxes by around six hours. Figure 5-20 showed that a lag was also discernable for soil temperatures measured closer to the surface (2.5 cm).

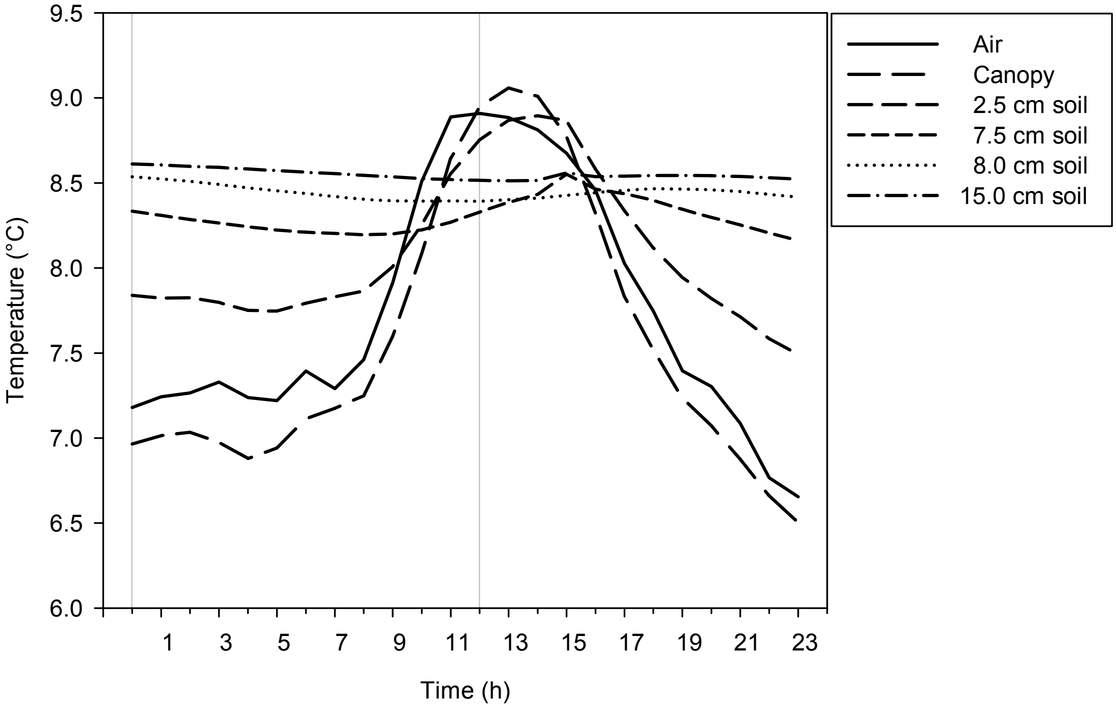


Figure 5-20: Daily courses of air and soil temperature measured at different depths (from 3 m air temperature to 15 cm below the peat surface). Hourly data points are means for the month of October 2006.

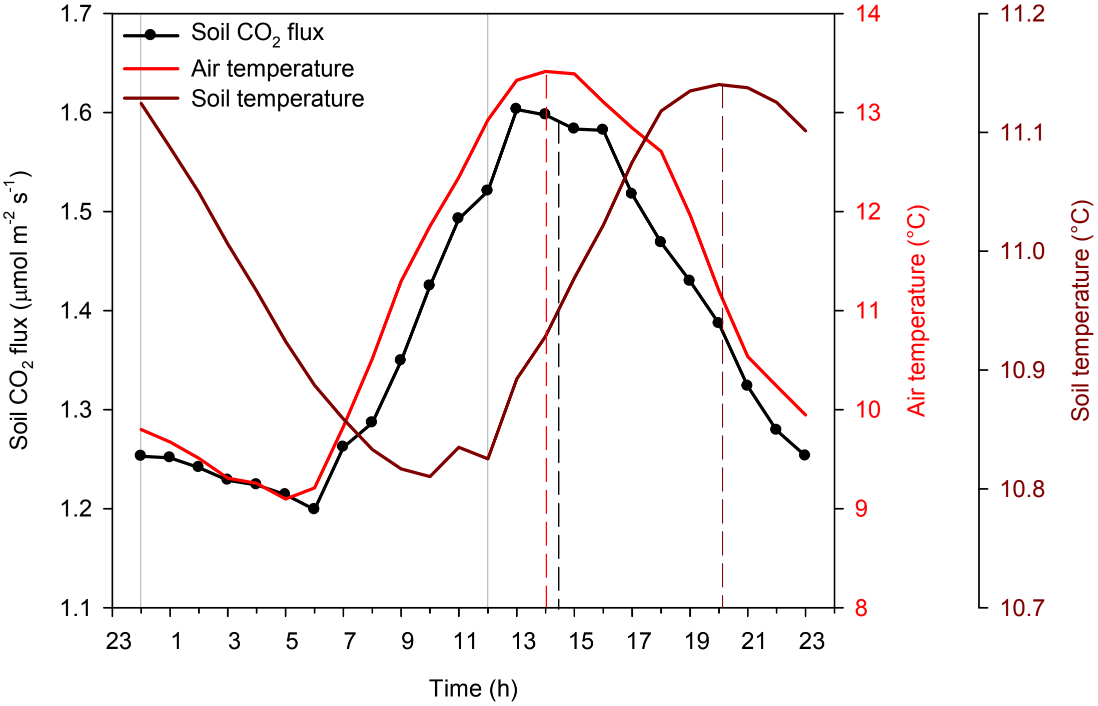


Figure 5-21: Daily courses of soil CO_2 flux, air and soil temperature. Hourly data points are means for the month of August 2006. Vertical dashed lines show the peak points of the daily cycles.

The temperature sensitivity of the soil CO_2 flux was estimated by calculating the Q_{10} function (Equation 5.9). Table 5-9 shows that the Q_{10} value was highly dependent upon the choice of temperature that was used in the calculation. Relatively good relationships can produce physically unrealistic values, and this is particularly the case when deeper soil temperatures are used. In the summer, the relationships were not particularly strong; it was demonstrated earlier that temperature was not the only factor affecting fluxes. Additionally, temperature data were not available from a full range of soil depths. A Q_{10} value of 1.90 was estimated from the relationship with air temperature, while the relationship with soil temperature at 8 cm yielded a biologically unrealistic value of 15.38. During the winter period, temperature data were available from a wider range of air and soil depths. Q_{10} estimates ranged from 2.55 to 5.74; in general the higher values were estimated from the deeper soil temperature measurements and values of around 2.55, which are closer to the literature consensus, were achieved with air and canopy temperature relationships. The two periods could only be compared in terms of their air temperature Q_{10} values, when winter time soil CO_2 fluxes were more sensitive to temperature than summer time fluxes.

Table 5-9: The temperature sensitivity of the soil CO_2 flux. The Q_{10} function is calculated separately for the two time periods and using different soil temperature depths and air temperature.

	R^2	Q_{10}
Summer period		
Air temperature	0.37	1.90
Soil temperature at 8.0 cm	0.40	15.38
Winter period		
Air temperature	0.63	2.55
Canopy temperature	0.69	2.57
Soil temperature at 2.5 cm	0.79	4.24
Soil temperature at 7.5 cm	0.76	5.74
Soil temperature at 8.0 cm	0.65	5.23
Soil temperature at 15.0 cm	0.55	5.12

5.3.6 An annual budget of soil CO_2 efflux

In order to estimate an annual budget for the soil CO_2 flux, small gaps, of the order of several days to weeks, in measurement record (July 2006 to March 2007) were filled using the summer and winter models. In addition to this, a further four and a half months of data were required to complete an annual cycle (March to July 2007). The year was split into the growing season (April to September) and the non-growing season (October to March) and models were separately parameterised using measurements from these two periods. The estimated total soil CO_2 flux for the annual period from 27 July 2006 to 26 July 2007 was 261.61 ± 52.04 g C m^{-2} yr^{-1} (Figure 5-22). This figure is a product of hourly measurements and modelled results and errors associated with each of these components were also calculated. For periods when measurements were taken, fluxes were usually available from nine chambers and a standard error term of ± 15.76 g C m^{-2} yr^{-1} was calculated for the annual period. A further error term to account for the uncertainty around the modelled results was calculated based on the model fit to the available data, for the whole period, this added an extra error of ± 36.28 g C m^{-2} yr^{-1}.

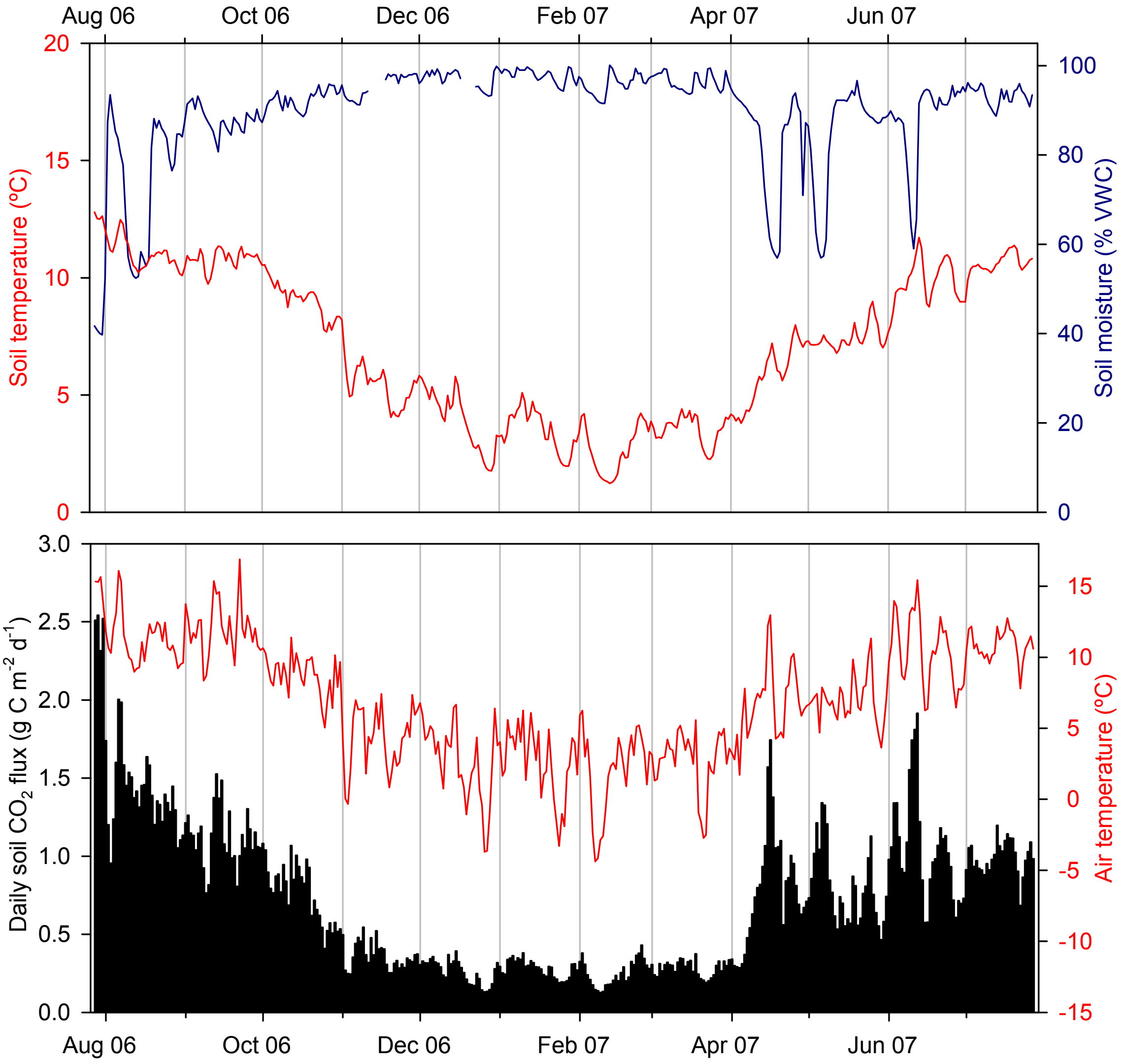


Figure 5-22: Mean daily soil CO_2 flux and environmental variables measured at Bog End, Moor House NNR, for the period 27 July 2006 to 26 July 2007. Soil CO_2 flux data are measured when available and the remainder are modelled results to complete an annual budget.

5.3.7 Time of measurement effects

The availability of continuous hourly measurements allowed an investigation into the effect of the time of measurement on the magnitude of the soil CO_2 fluxes measured. Whole day fluxes were assumed to be the closest to the actual daily flux being the sum of 24 hourly measurements; Middle day fluxes assumed that measurements taken during the hours of 11:00 and 15:00 could be simply applied to the whole day and Peak hour fluxes assumed that measurements taken between 12:00 and 13:00 could be applied to the whole 24 hours. During the summer months of July to September, the mean daily fluxes were highest when calculated from Peak hour measurements and decreased in the order: Peak hour > Middle day > Whole day (Table 5-10). However, these differences were only significant for the month of July (Table 5-11; $p < 0.05$) when the mean Whole day total of 2.31 ± 0.15 g C m^{-2} d^{-1} was significantly less than the mean Peak hour total of 2.94 ± 0.39 g C m^{-2} d^{-1} ($p < 0.05$). The mean values obtained using the three calculation methods were remarkably similar for the winter months of October to February, often not differing at all (Table 5-10). Between-within subjects ANOVA tests showed that there were no significant differences for these months (Table 5-11; $p > 0.05$ in all cases).

Table 5-10: Total daily soil CO_2 fluxes (g C m^{-2} d^{-1}; mean ± one standard error) for eight months during 2006 and 2007. Whole day fluxes are the sum of 24 hourly measurements; Middle day fluxes are based on measurements taken between 11:00 to 15:00 and Peak hour fluxes are based on measurements taken between 12:00 and 13:00 (All times are GMT).

Date	Whole day	Middle day	Peak hour
July 2006	2.31 ± 0.15	2.70 ± 0.30	2.94 ± 0.39
August 2006	1.41 ± 0.04	1.61 ± 0.05	1.64 ± 0.06
September 2006	1.12 ± 0.04	1.27 ± 0.04	1.28 ± 0.04
October 2006	0.56 ± 0.02	0.56 ± 0.02	0.54 ± 0.03
November 2006	0.37 ± 0.02	0.37 ± 0.02	0.37 ± 0.02
December 2006	0.27 ± 0.02	0.27 ± 0.01	0.27 ± 0.01
January 2007	0.31 ± 0.01	0.31 ± 0.01	0.31 ± 0.02
February 2007	0.27 ± 0.02	0.28 ± 0.02	0.28 ± 0.02

Table 5-11: Results from one-way repeated measures ANOVA with between-subjects comparisons testing the effects of measurement period on daily soil CO_2 fluxes. The total daily flux based on the sum of 24 hourly measurements was compared to daily fluxes calculated from an average of middle-day fluxes (11:00 to 15:00) as well as those based on peak hour fluxes (13:00).

Source of variation	*F*	d.f.	*p*
July 2006			
Within-subjects			
Time	56.847	4.000	0.000
Time × measurement period	2.527	8.000	0.024
Between-subjects			
Measurement period	3.738	2.000	0.039
August 2006			
Within-subjects			
Time	13.991	3.308	0.000
Time × measurement period	0.676	6.616	0.684
Between-subjects			
Measurement period	0.565	2.000	0.576
September 2006			
Within-subjects			
Time	8.316	3.047	0.000
Time × measurement period	0.341	6.094	0.915
Between-subjects			
Measurement period	0.661	2.000	0.525
October 2006			
Within-subjects			
Time	12.828	4.711	0.000
Time × measurement period	0.441	9.422	0.916
Between-subjects			
Measurement period	0.047	2.000	0.954
November 2006			
Within-subjects			
Time	11.160	2.380	0.000
Time × measurement period	0.158	4.761	0.973
Between-subjects			
Measurement period	0.001	2.000	0.999

Continued on Page 135

Continued from Page 134

Source of variation	*F*	d.f.	*p*
December 2006			
Within-subjects			
Time	3.807	1.923	0.034
Time × measurement period	0.181	3.846	0.942
Between-subjects			
Measurement period	0.016	2.000	0.985
January 2007			
Within-subjects			
Time	5.765	2.286	0.005
Time × measurement period	0.375	4.573	0.848
Between-subjects			
Measurement period	0.003	2.000	0.997
February 2007			
Within-subjects			
Time	20.895	2.458	0.000
Time × measurement period	0.142	4.916	0.980
Between-subjects			
Measurement period	0.117	2.000	0.890

5.4 Discussion

5.4.1 Spatial variation

There was a high degree of variation in the magnitude of the soil CO_2 fluxes that were measured during several hours along a transect through the typical Calluneto-Eriophoretum plant community that dominates the Bog End study site (coefficients of variation of 37 to 54 %). Luo and Zhou (2006) collated equivalent CV values, these varied from similar values of 35 % for grasslands, to highly varied figures for temperate forests (10 to 100 %), and to extremely high values from agricultural fields (150 %). A pattern common to many soil properties is that there will be a degree of spatially-dependent variation, in that measurements taken closer together are more likely to be similar to one another than those from points which are further apart. In a peatland, it might be hypothesised that spatial patterns of vegetation type, topography, peat depth and hydrology, for example, would contribute to corresponding spatial patterns of soil CO_2 fluxes. Geostatistics were used in an attempt to identify spatially-dependent variation and the scale at which it might be operating. At scales of 5 m, 1 m and at a finer scale of 0.25 m, there was no evidence of any spatially-dependent variation along the transect. There are perhaps two explanations for this: the first being that any spatially-dependent variation was acting at a finer scale than that measured. Alternatively, the pattern might be a result of largely similar fluxes, matching the homogenous pattern of the vegetation composition, interspersed with almost random hotspots of relatively high or low fluxes. A more detailed study of the landscape-scale spatial variation of soil CO_2 fluxes might have included more transects or a grid sampling design across the area. This is a highly time- and labour-intensive data collection procedure, especially considering that ideally there would not be a great time difference in-between measurements. Nevertheless, this study provided evidence that it was justifiable to place the long-term measurement chambers within a 20 m diameter area, which was the limit of the automated system, in order to capture the landscape scale variation.

5.4.2 Vegetation type and soil CO_2 fluxes

Long-term soil CO_2 flux chambers were placed within each of the three vegetation type patches to test if vegetation type influenced soil CO_2 fluxes. The mean data presented in

Figure 5-7 suggests that there may have been an effect with fluxes appearing to be consistently lower from the Moss plots than from both the *Calluna* and *Eriophorum* plots. However, these differences were found to be not significant and largely a result of consistently depressed fluxes from a single Moss plot which was not replicated among the other plots. One hypothesis was that fluxes would have been lower from the Moss plots, in part as a result hydrology. The Moss patches, dominated by *Sphagnum* spp., might have been expected to dominate wetter areas with higher soil moisture and associated lower soil temperatures. In turn, these linked biological – environmental factors could have driven differences in the soil CO_2 fluxes. The data actually showed that there were no significant differences in soil moisture or temperature between the different vegetation plots. An alternative hypothesis is that fluxes might have differed as a result of different root distributions. *Calluna* and *Eriophorum* roots would contribute to the autotrophic component of the soil CO_2 flux while also stimulating heterotrophic respiration with a supply of labile carbon. These are processes that would not be associated with the Moss vegetation. However, as no significant differences were observed, there was no support for this hypothesis. As the different above-ground vegetation patches were relatively small, the likelihood is that there would be a degree of root colonisation from plants of one type into the soil space of the other types, in particular exploiting the soil space of the Moss patches. Had significant differences in fluxes been found, this would have warranted further investigation into the root distributions of the vegetation types.

Studies where there have been more distinct differences in plant communities have showed significant differences in soil CO_2 flux rates. In a mixed conifer forest, adjacent areas of woody vegetation and scattered herbaceous vegetation exhibited different soil CO_2 flux rates, which were attributed to differences in the fine root and rhizomorph dynamics associated with the vegetation type (Rodrigo Vargas, 2008). McNamara *et al.*, (2008) found significantly higher ecosystem respiration fluxes from gully areas compared to the Calluneto-Eriophoretum plant community at Moor House. Also working at Moor House, and studying net CO_2 fluxes as opposed to soil CO_2 fluxes, Ward *et al.*, (2009) showed that plant functional group was a significant factor. They found that removing ericoid dwarf-shrubs caused increased rates of GPP and ER relative to a control, which they attributed to the slow growing, nutrient-poor and phenolic-rich nature of the ericoid tissues.

Since the analysis in this study failed to identify significantly different fluxes from the different vegetation patches, it was decided to pool the data, interpreting the variation as that naturally occurring within the landscape. Had significant differences been found, data from a vegetation survey (Table 5-1) would have allowed a simple exercise to scale the measured fluxes to the estimated areal coverage of the different vegetation types.

5.4.3 Diurnal cycling and time of measurement effects

Soil CO_2 flux followed a diurnal cycle during the summer months (July to October), peaking during the afternoon. The greatest range occurred in July, when night time fluxes were on average around 1 μmol m^{-2} s^{-1} lower than peak day time fluxes. The greatest difference measured was 2.22 μmol m^{-2} s^{-1}. These clear cycles were not apparent during the winter months (November to February).

Linked to the above findings, the study provided evidence that estimates of soil CO_2 flux based on manual surveys require careful interpretation. Such survey measurements will often be taken during the hours around midday. This study benefitted from the availability of high temporal resolution hourly data for months from July through to February. These data allowed the calculation of a best estimate of the true daily total CO_2 flux of the site. To compare this figure to those that would have been yielded by a more traditional manual sampling regime, a 'Middle day' figure was generated from an average of measurements taken during the middle of the day (11:00 – 16:00) and a 'Peak hour' figure was based on measurements made between 12:00 and 13:00. During the growing season months (July to September) the daily fluxes were between 27 % (July) and 14 % (September) higher using middle day and peak hour measurements when compared to the estimates made with a whole day of measurements. This difference was significant for the July data, while for the remaining winter months (October to February) the three estimates were remarkably similar. This is a feature of the seasonal variation in the strength of the diurnal pattern of the soil CO_2 flux. During the winter, when there was little evidence of a diurnal cycle, measurements taken during the middle of the day provided a sufficient basis for calculating daily total fluxes. In summer months, when stronger air and near-surface soil temperature fluctuations drive stronger diurnal cycles of soil CO_2 flux, simply applying middle day measurements to the rest of the day resulted in a significant overestimation of the daily fluxes (cf.Crill, 1991; Glenn *et al.*, 2006). A possible approach to overcome this problem would be based on modelling the fluxes for the non-measured hours of the day (Silvola *et al.*, 1996). However, it is unlikely that measurements would exist for the range of night-time environmental conditions, risking a situation where one would be forced into extrapolating out of the range of the available driving data.

5.4.4 Environmental drivers

It was assumed *a priori* that the primary factors determining the temporal variation of the soil CO_2 flux would be temperature or soil moisture or some combination of those two. During the winter, soil moisture was rejected as a potential controlling factor, as there was no significant relationship between it and soil CO_2 flux. This latter finding was not surprising, as soil moisture values were consistently close to saturation, never dropping below 90 % VWC during the whole period. Soil temperature was the most important factor, explaining 80 % of the variation in hourly soil CO_2 fluxes. For the range of temperatures encountered, the relationship followed a largely exponential response. A number of other commonly applied models were fitted to the data; these have been suggested to introduce a greater degree of reality to the temperature response. The Arrhenius model performed worst of all, failing to capture the continuing increase in fluxes at the highest temperatures. The Lloyd & Taylor model was very similar to the simple exponential model but performed marginally better and was the preferred model for describing the relationship and gap-filling.

The situation was more complex during the summer period, there was evidence that both temperature and soil moisture were playing a role in regulating the soil CO_2 flux. The same range of soil temperature data from different depths were not available, but both air and soil temperature at 8 cm explained a far lower proportion of the variation than either had during the winter period, 37 % and 40 % respectively. However, this could in part be explained by considering soil moisture; there was a significant negative relationship, showing lower fluxes when soil moisture was higher. There was also evidence that this effect was strongly driven by a drought period in July 2006. Some of the highest fluxes were measured when soil moisture dropped to around 40 % VWC and the relationship was weaker when these points were excluded. This, and the lack of an effect in winter, suggests that there is a threshold value below which soil moisture becomes an important regulator of the flux. Plotting the residuals of the preferred temperature model against soil moisture suggested that the effect persisted after temperature was accounted for. The model driven by temperature alone tended to underestimate the fluxes when the peat was dry and overestimate when the peat was wetter. A situation can be envisaged whereby temperature is controlling the rate of soil CO_2 flux, but under certain circumstances, this response is modified by the moisture status of the peat. For example, a period of drought causes the water table to drop and the peat to dry out and under these circumstances soil respiration will be more responsive to simultaneously occurring warm temperatures. A multiple regression model incorporating both temperature and soil moisture was a considerable improvement upon either of the single facto models, able to explain around 75 % of the variation. Working in quite different ecosystems, a well drained subalpine forest, Scott-Denton *et al.*, (2006) found that moisture status can modify temperature responses in a different way, when drought conditions caused a suppression of rates at higher temperatures.

The supposedly more physically-based Lloyd & Taylor model performed only marginally better during the winter period and offered no improvement over the simple exponential model. Lloyd and Taylor (1994) introduced their model, which is based on the Arrhenius model, but with the addition of a third parameter to account for the declining temperature sensitivity of soil respiration as temperature increases. They found that their model provided an unbiased estimate and improved model fit to data collected from a wide range of ecosystem types. It is suggested that in the present study, the development of separate seasonal models and the nature of the site meant that the soil temperature ranges were relatively small. Under these conditions, it is possible that the temperature sensitivity changes along the course of the relationship were small, thus negating the potential advantages provided by the Lloyd & Taylor model.

There has been some discussion in the recent literature regarding the role of soil temperature depth in determining the apparent temperature sensitivity. Soil temperature varies with depth, both in terms of dampened amplitudes and phase shifts with depth and because of this the calculated, apparent temperature sensitivity is highly dependent upon which depth temperature is measured. This effect, which results in an increased apparent Q_{10} with depth has been noted in several recent studies (Pavelka *et al.*, 2007;

Reichstein *et al.*, 2005; Xu & Qi, 2001) and is now also seen in this present peatland study. A number of methods have been used to determine which the most appropriate temperature depth to choose is; including the relationship yielding the highest R^2 (Pavelka *et al.*, 2007) and that with the lowest hysteresis between temperature and flux cycles (Gaumont-Guay *et al.*, 2006). Pavelka *et al.*, (2007) conclude by recommending that the most accurate Q_{10} values require soil temperatures to be measured at very shallow depths and preferably at the soil surface. This feature and the fact that historically, a whole range of soil temperature depths have been used in the Q_{10} calculations means that comparisons between studies in the literature must be treated with some caution (Herbst *et al.*, 2008). In the present study, air, canopy and near soil surface temperatures yielded the highest R^2 values and also Q_{10} values that are generally interpreted as typical of most ecosystems (Davidson *et al.*, 2006; Raich & Schlesinger, 1992).

The available data in the present study only allowed the comparison between summer and winter seasons of Q_{10} values calculated from air temperatures and soil temperatures at 8 cm depth. The summer time Q_{10} from soil temperatures yielded an unrealistically high value that is sometimes the result of deeper soil temperature measurements (Pavelka *et al.*, 2007). Air temperature Q_{10} values suggested that the soil CO_2 flux was more sensitive to temperature during the winter period than in summer. This may be due to the influence of soil moisture, Silvola *et al.*, (1996) found higher Q_{10} values in boreal mires when tater tables were higher compared to when they were below 20 cm.

Temperature, and under certain circumstances soil moisture, are the primary drivers of the variation in soil CO_2 fluxes; but theory suggests that other environmental variables should have a significant and detectable influence on the magnitude of measured fluxes. In particular the supply of photosynthates to the roots and rhizosphere in general will vary temporally; in particular it is likely to increase following periods of higher assimilation by the above-ground vegetation (Bahn *et al.*, 2008; Bahn *et al.*, 2009; Liu *et al.*, 2006; Tang *et al.*, 2005). As such there would be an indirect link between photosynthetically active radiation (PAR) and soil CO_2 fluxes. The high temporal resolution data set obtained through this study would be ideal to investigate this potentially controlling pathway. However, a significant problem is associated with separating the often covarying factors of temperature and PAR. Liu *et al.* (2006)

proposed a method which relied on first calculating a temperature-dependent component of the soil CO_2 flux (R_t) by fitting a soil temperature-based model to the data. The residuals of this relationship were taken to be a temperature-independent component (R_i) and they identified a relationship between this temperature-independent flux and the diel cycle of available PAR. The authors hypothesised that photosynthesis was driving a separate, temperature-independent diel cycle of soil respiration. However, as others have noted, this method is susceptible to the confounding effects of the choice of soil temperature (Bahn *et al.*, 2009). The model would produce a peak R_t flux whenever soil temperature peaked and as this study showed (Figure 5-21) that this time would be highly variable depending on which soil temperature data were used. When the R_i component is based on subtracting the modelled R_t flux from the total flux, then the presence or absence, timing and magnitude of R_i becomes dependent upon which soil temperature data were used for the R_t model.

While it was originally intended to follow the above routine to quantify the role of photosynthesis in controlling the soil CO_2 flux, these drawbacks cast doubt on the methodology. Identifying the link between carbon inputs into the soils and fluxes to the atmosphere is nevertheless an important goal (Davidson *et al.*, 2006). Improved understanding in this respect will show when and where this is an important process to consider and in the future it may be incorporated into the next generation of process based models of soil CO_2 flux that move beyond simple empirical relationships with temperature and moisture. Tang *et al.*, (2005) combined measurements of productivity with soil CO_2 flux measurements both under trees and in the open, they found evidence of tree photosynthesis modulating the diurnal cycle of soil CO_2 fluxes. While soil CO_2 fluxes in the open were driven by temperature, fluxes beneath trees were decoupled from temperature but correlated well with tree photosynthesis with a time lag of 7-12 hours. Currently stable isotope studies are providing some of the more robust insights: Bahn *et al.*, (2009) found that the products of photosynthesis provided an important and immediate source of carbon to the soil respiratory fluxes.

5.4.5 Model development, seasonal and annual budgets

During the measurement period from the end of July 2006 to the beginning of March 2007, hourly measurements were available for the majority of the time. Some gaps existed due to equipment failure and a three week period when the automated chamber system was used for a separate experiment. The relationships with environmental variables described in the previous section were used to construct models, the output of which could be used to estimate the soil CO_2 fluxes for the gap periods. This period of just over seven months and including the winter months of 2006/07 represented a substantial source of carbon to the atmosphere, of 147.48 ± 22.91 g C m^{-2}.

Raich and Schlesinger (1992) produced a comprehensive assessment of soil respiration fluxes from a range of global ecosystems using literature values. Their estimates included 60 ± 6 g C m^{-2} yr^{-1} for tundra, 94 ± 16 g C m^{-2} yr^{-1} for northern bogs and mires and 713 ± 88 g C m^{-2} yr^{-1} for Mediterranean woodlands and heaths. The latter included several references from *Calluna* heaths in northern Europe.

Over the 17 years since the Raich and Schlesinger publication, there have been a great many studies addressing the role of soil CO_2 fluxes in a wide range of ecosystems, meaning that there is a wealth of further data available, although there has been no attempt to produce an updated version of Raich and Schlesinger's database. Indeed, more recent reviews of the subject (e.g. Davidson *et al.*, 2006) continue to cite Raich and Schlesinger's figures as the best available synthesis. A literature search reveals however, a surprising lack of relevant studies from comparable peatland ecosystems. The literature is dominated by studies carried out in forest ecosystems, where the focus has been on quantifying the role of soil CO_2 fluxes in releasing sequestered carbon from the system (Heath *et al.*, 2005). A literature search including the terms: "Soil respiration" OR "Soil CO_2 flux" AND Forest* yielded 1592 returns while one using the terms: "Soil respiration" OR "Soil CO_2 flux" AND Peat* returned just 109 publications (Web of Knowledge (www.isiknowledge.com); accessed 14 August 2009). Indeed, a number of estimates cited in Table 5-12 are actually from studies on forested peatlands. With the availability of eddy covariance systems, there appears to have been an emphasis on measuring the net fluxes of CO_2 and also determining ecosystem respiration, but there are far fewer examples of recent studies which have sought to produce seasonal or annual budgets of soil CO_2 fluxes in peatlands.

The earlier figure of 147.48 ± 22.91 g C m^{-2} was calculated for the measurement period, but it was desirable to estimate the annual flux for comparison with other ecosystems and peatlands. The soil CO_2 flux models that were parameterised using the 2006 to 2007 data and used for gap-filling were applied to the remaining months of March to July 2007 to make up a full annual cycle. The annual figure of 261.61 ± 52.04 g C m^{-2} yr^{-1} from this study is unsurprisingly higher than Raich and Schlesinger's estimate for northern bogs and mires, the majority of the contributing sites were relatively high latitude sites in Canada and Alaska (Moore & Knowles, 1989). A number of the studies in Table 5-12 were carried out on forested peatlands, where we might expect lower water tables and the input of tree-derived photosynthates to be driving the higher soil CO_2 fluxes that have been observed (Mäkiranta *et al.*, ; Minkkinen *et al.*, 2007). It is worthy of note that factors contributing to the relatively high total flux were summer periods when drought conditions combined with high temperatures causing daily fluxes of up to 2.6 g C m^{-2} d^{-1}. Winter time fluxes also made important contributions to the annual flux, daily fluxes were always positive even when daily air temperature dropped below 0 ºC and during the coldest months of January and February, daily fluxes were often close to 0.5 g C m^{-2} d^{-1}.

Table 5-12: Annual soil CO_2 fluxes (g C m^{-2} yr^{-1}) for Moor House and a range of peatlands and other similar ecosystems for comparison.

Ecosystem	Site	Location	Lat/Long	Soil CO_2 flux	Time period	Method	Reference
Minnesota peatland	Chippewa	Minnesota	47° 32’ N, 93° 28’ W	362 [~]	1991	Closed-chamber	(Kim and Verma, 1992)
Lowland heath	Dorset dunes	Southern England	50° 40’ N, 01° 55’ W	1010.00	1972 - 1973	Alkali absorption	(Chapman, 1979)
Blanket bog	Moor House	Northern England	54° 41’ N, 02° 21’ W	262	2006 - 2007	Closed-chamber	This study
Forestry-drained fen [1]	Väätsaä	Central Estonia	58° 59’ N, 25° 27’ E	376 [#]	2003	Closed-chamber	(Minkkinen *et al.*, 2007)
Afforested peatland	Various	Southern Finland	-	207 - 539	2002 - 2005	Closed-chamber	(Makiranta *et al.*, 2007)
Forestry-drained mire [2]	Vesijako	Southern Finland	61° 22’ N, 25° 07’ E	248 [#]	2002 - 2004	Closed-chamber	(Minkkinen *et al.*, 2007)
Ombrotrophic mire [3]	-	Southern Finland	-	60 - 200	1991 - 1992	Closed-chamber	(Silvola *et al.*, 1996)
Ombrotrophic mire [4]	-	Southern Finland	-	290 - 340	1991 - 1992	Closed-chamber	(Silvola *et al.*, 1996)
Cutaway peatland	Aitoneva	Central Finland	62° 12’ N, 23° 19’ E	276 - 479	2002 - 2005	Closed-chamber	(Makiranta *et al.*, 2007)
Forestry-drained fen [5]	Kivalo	Northern Finland	66° 21’ N, 26° 37’ E	515 [#]	2002 - 2004	Closed-chamber	(Minkkinen *et al.*, 2007)
Tundra	Kolyma	Siberia	-	105 - 144	1990	Closed-chamber	(Fedorov-Davydov, 1998)

[1] With 40 year old Scots pine (*Pinus sylvestris*) plantation

[2] Managed as a plantation since 1915

[3] A range of Sphagnum dominated sites between latitudes 61 47 N and 62 46 N.

[4] A range of mires with abundant under-storey vegetation between latitudes 61 47 N and 62 46 N.

[5] Managed as a plantation since 1933

[~] For the six-month period from May to October

[#] Heterotrophic flux only

5.1 Summary

This study used high temporal resolution hourly data and empirical models to produce the first annual soil CO_2 flux budget for a UK peatland. During a just greater than seven month period, from July 2006 to March 2007, an estimated 147.48 ± 22.91 g C m^{-2} was respired from the soils to the atmosphere. The application of simple seasonal models allowed the fluxes to be predicted for the remaining five months, to complete a full annual cycle, yielding a figure of 261.61 ± 52.04 g C m^{-2}.

There was no evidence of spatially-dependent variation in the soil CO_2 flux; at the scales measured, fluxes were no more likely to be similar close together than further apart.

The Calluneto-Eriophoretum plant community is largely composed of patches of three vegetation types; *Calluna*, *Eriophorum* and 'Moss spp.'. CO_2 fluxes were not significantly different from the soils within the different vegetation patches.

During the summer months, the soil CO_2 flux exhibited a clear diurnal cycle, peaking in the afternoon, which was absent during the winter months. This showed the advantages of continuous, automated monitoring and has implications for studies relying on manual survey measurements made during the middle of the day. In July, simply interpolating mid day measurements to the rest of the day resulted in a significant over-estimate of the daily flux.

Winter soil CO_2 fluxes were strongly driven by variations in soil temperature; during these months, the peat was constantly close to saturation and there was no evidence of a soil moisture effect. The situation was more complex during the summer; the relationships with temperature were less strong and there was evidence that soil moisture was playing a role in controlling the fluxes. In particular, fluxes were higher than expected from a simple temperature model during a drought period and it seems that low soil moisture conditions allowed a considerable increase in the soil respiratory processes. Summer time fluxes were best described by a multiple regression model incorporating both temperature and soil moisture.

CHAPTER 6

METHANE FLUXES AT THE LANDSCAPE SCALE

6.1 Introduction

6.1.1 Scope

The carbon balance of most terrestrial ecosystems is determined by the relative strength of the net gaseous CO_2 flux and its components. The unique conditions found in peatlands means that other carbon flux pathways exist and these can be vital when considering the whole carbon budget of a site/locality (Minkkinen *et al.*, 2002, Wille *et al.*, 2008). These include various fluvial fluxes, whereby significant quantities of organic matter are eroded and transported out of the system, and the flux of methane from the peat soils to the atmosphere. The earlier chapters of this thesis have investigated the various gaseous CO_2 fluxes at Moor House NNR and other studies have quantified the fluvial fluxes (Warburton *et al.*, 2004, Evans and Warburton, 2005, Worrall and Burt, 2005, Worrall *et al.*, 2005); this sixth chapter addresses the size and controls on the methane flux.

Northern wetlands and tundra are a significant source of methane, contributing about 20 % of the annual global emissions (Gorham, 1991). Whilst fluxes from individual sites may be smaller than those of CO_2, the fact that methane has a global warming potential 25 times greater than that of CO_2 (IPCC, 2007) means that relatively small fluxes can become significant in terms of landscape greenhouse gas budgets.

Methane is produced by methanogenic microbes as the end product of anaerobic decomposition, in peatlands. This activity is concentrated below the water table in the anaerobic catotelm region (Blodau, 2002). Following production, methane may then be released to the atmosphere via one of three pathways: diffusion, via aerenchymatous vascular plants or via ebullition (Blodau, 2002). Spatial variation within peatlands of factors which affect the methanogenic production and gas transport, such as water level, vegetation structure and pH, mean that there can be considerable spatial variation in the magnitude of the methane fluxes (Laine *et al.*, 2007).

Many studies have identified considerable temporal variation in fluxes at a range of scales. Seasonal variation is strong, driven by soil temperature and water table depth (Saarnio *et al.*, 1997) and some studies have reported small, but significant, winter-time fluxes (Laine *et al.*, 2007, Rinne *et al.*, 2007). Some studies have identified a diurnal cycle, with fluxes peaking during the day (Fowler *et al.*, 1995, Suyker *et al.*, 1996, Kim *et al.*, 1998), whilst others have not (Kormann *et al.*, 2001, Rinne *et al.*, 2007). These contrasting findings are likely due to differing degrees of diurnal variation in the controlling soil temperature (Fowler *et al.*, 1995, Hargreaves and Fowler, 1998) or the presence of vegetation types which may be responsible for facilitating methane transport at different times of the day (Chasar *et al.*, 2000).

Eddy covariance studies of methane fluxes have traditionally lagged behind those of CO_2 fluxes, both in terms of number and the length of measurement periods. This is in part due to the relatively labour-intensive effort required to obtain continuous 'automated' measurements and the expensive equipment required. Nevertheless, the technology has existed for several decades now and early studies often reported short-term campaign measurements from a range of northern wetlands (Verma *et al.*, 1992, Edwards *et al.*, 1994, Clement *et al.*, 1995, Suyker *et al.*, 1996, Billesbach *et al.*, 1998, Kim *et al.*, 1998, Hargreaves *et al.*, 2001). More recently, records extending throughout the growing season have been published from tundra sites (Sachs *et al.*, 2008, Wille *et al.*, 2008) and a complete annual cycle has been measured at a boreal fen in Finland (Rinne *et al.*, 2007).

Studies involving the blanket bogs typically found in the British Isles are limited. Early, short-term, campaign measurements over blanket bog sites in Caithness, Scotland found that the peatlands there were a source of methane and they established relationships with temperature and water table depth (Fowler *et al.*, 1995, Beverland *et al.*, 1996, MacDonald *et al.*, 1998). Hargreaves and Fowler (1998) used a limited summer-time data set to produce an estimate of the annual flux of 5.16 g C m^{-2} yr^{-1}. More recently, Laine *et al.* (2007) used the data from two years of chamber measurements to produce an annual estimate of 4.5 g C m^{-2} yr^{-1} for an Irish lowland blanket bog. Some data do exist from Moor House NNR, but these are studies quantifying the spatial variation and land management effects on methane fluxes. They do, nevertheless, suggest that blanket bog can act as a methane source (Ward *et al.*, 2007, McNamara *et al.*, 2008). Further work to contribute towards a more complete carbon budget for Moor House and to explore the environmental controls on the methane flux from upland blanket bogs is warranted.

6.1.2 Aims

The previous three chapters have addressed various aspects of the CO_2 fluxes between the land surface and atmosphere over the blanket bog site at Moor House. Here the focus moves to methane, another potentially important carbon flux within peatland ecosystems; the following research questions are addressed:

- Is the blanket bog at Moor House a significant source of methane?
- Do methane emissions follow a diurnal cycle?
- What are the important environmental factors driving the variation in methane fluxes?
- Can a model be produced to extend the measurement record and produce seasonal or annual methane budgets?
- And finally, how much carbon is emitted from the peat as methane during an annual cycle?

6.2 Methods

6.2.1 Field site

Measurements were again taken at the Bog End area of the Moor House reserve (54° 41’ 27” N, 02° 21’ 50” W; 564 m elevation) and the site is described in detail in Section 2.4.

6.2.2 Eddy covariance measurements

An eddy covariance system to measure the flux of methane was mounted on the same 3 m high flux tower as was used to make the CO_2 flux measurements described in Chapter 3. In addition to the CSAT3 sonic anemometer (Campbell Scientific Inc, Logan, Utah, USA) to measure the vector components of the wind, which was already in place, a tunable diode laser spectrometer (TGA 100A, Campbell Scientific Inc.) for methane concentration analysis was added to the system. The air sample intake was located 20 cm behind the path length of the sonic anemometer. A vacuum pump drew the sample air at rate of 15 L min^{-1} from the intake and through a reversed flow membrane gas dryer before entering the closed path gas analyser itself. The TGA100A also requires a constant flow of a reference gas (1.0 % CH_4), which was supplied by a calibrated gas bottle. The instrument calibration was checked using a zero (N_2) and span gas (1.88 ppm CH_4) at the start of the first and third measurement campaigns. The TGA100A was supplied in a weather-proof, and temperature controlled, enclosure which was placed at the base of the flux tower. The diode laser itself is mounted within a liquid nitrogen laser Dewar, which was topped up with liquid nitrogen every six days to maintain the necessary cold conditions around the laser.

Raw data outputs from the sonic anemometer and TGA100A were logged continuously at a frequency of 10 Hz by a CR5000 datalogger (Campbell Scientific Inc.). The datalogger also ran a program which generates on-line half-hourly fluxes and stores these alongside half-hourly measurements of the environmental variables. Full details of all ancillary measurements made and the instruments used can be found in Section 3.2.2.

In theory, the TGA100A offers the opportunity to collect long-term, continuous measurements of methane fluxes in the field. In reality, in many instances, measurement time is limited by power requirements and the need for regular attention by the operator. For this reason, measurements were made in ‘campaign’ mode with the aim of capturing as much of the annual variation in fluxes and environmental conditions as possible. To this end a summer campaign ran for from 24 July to 11 August 2007 and two autumn campaigns covered 15 October to 25 October 2007 and 01 November to 12 November 2007, giving a total of 42 days of data.

6.2.3 Data processing

The EdiRe software was used to post-process the data, apply corrections and calculate fluxes (John Moncrieff & Robert Clement; University of Edinburgh). The complete processing list used to calculate fluxes at Bog End is included in Appendix 1, but a description of the routine follows below.

Fluxes of methane were calculated as the covariance of the deviations from the mean of the vertical wind velocity and scalar concentrations following the methodology set out by Aubinet *et al.* (2000). Following Billesbach *et al.* (1998) and Sachs *et al.* (2008) an averaging interval of 60 minutes was used for the covariance calculations in order to reduce the signal to noise ratio present as a result of the relatively low fluxes at the site. The high-frequency raw data streams were first subject to a despiking routine similar to Hojstrup (1993), based on standard deviation from the hourly mean. A planar fit coordinate rotation was applied to the three velocity components (Wilczak *et al.*, 2001), and sonic anemometer air temperature was corrected for humidity fluctuations (Schotanus *et al.*, 1983). Frequency response corrections to account for sensor path lengths, sensor separation and tube attenuation effects were applied to the methane flux (Moore, 1986). The friction velocity was calculated as a measure of the degree of turbulent mixing and this was used to determine if there was evidence of the underestimation of fluxes during periods when the assumptions of the eddy covariance method were not met.

The hourly fluxes showed a relatively large variation even after extending the averaging period and filtering out data associated with low turbulence, this included some negative values. Several other studies using the same instrument and similar processing routines have also encountered this phenomenon (Rinne *et al.*, 2007, Sachs *et al.*, 2008, Wille *et al.*, 2008). In common with the site used in this study, these workers did not expect their sites to exhibit significant levels of methanotrophy and the values have been attributed to "the relatively large random uncertainty of a single half-hourly flux value when measuring low fluxes" (Rinne *et al.*, 2007) and "generally low methane fluxes and high wind speeds at our site, and an insufficient suppression of concentration drift in the methane concentration signal" (Sachs *et al.*, 2008). However, there is no consensus regarding the treatment of these fluxes. Wille *et al.* (2008) and Sachs *et al.* (2008) found that applying a filter based on the signal to noise ratio of the flux calculation effectively removed all negative values, while Rinne *et al.* (2007) included the points in further analysis.

The sign convention is such that positive values indicate a flux away from the surface and negative values show a flux towards the surface.

6.2.4 Chamber measurements

Four vegetation types were identified within the flux footprint, *Calluna* and *Eriophorum* represented the majority of the landscape, whilst the wet *Sphagnum* and *Juncus* plots represented small areas of the flux footprint, but were included in the sampling strategy because previous studies have shown that these areas may act as methane emission 'hot-spots'. Plots within each of the four vegetation types were randomly located within a sector south-west and up to a distance of 120 m from the flux tower (n = 3 for *Sphagnum* and *Juncus* plots and n = 5 for *Calluna* and *Eriophorum* plots).

Prior to measurement, PVC measurement collars (20 cm diameter; 15 cm height) were installed at each plot, by cutting the peat to a depth of 5 cm and pressing the collar down. At the start of the measurement period, dark static gas sampling chambers (20 cm diameter; 40 cm height) were placed over the collars and sealed with a rubber gasket. Chambers were closed for a 20 minute period and during this time, four (20 ml) head space gas samples were extracted (at 0, 5, 10 and 20 minutes) and transferred to gas tight Exetainers (Labco Ltd., UK).

On return to the laboratory, methane concentrations of the samples were analysed using a PerkinElmer Gas Chromatograph (PerkinElmer, Waltham, Massachusetts, USA). Fluxes (mg m^{-2} h^{-1}) were calculated from the linear change in methane concentrations over the measurement period.

6.2.5 Modelling and uncertainty analysis

The simple exponential model (van't Hoff, 1884) was used to describe the temperature response of daily methane fluxes:

$$\mathrm{CH_4\ flux} = R_b e^{\beta T} \quad \mathbf{(6.1)}$$

where, T is temperature and R_b and β are both fitted parameters > 0. Parameters were fitted by minimising the root mean square error (RMSE) using the Solver function in Microsoft Office Excel 2007 (Microsoft Corporation, Redmond, Washington, USA).

The temperature sensitivity of the methane flux was assessed by the Q_{10} factor. This is the factor by which methane production is multiplied when temperature increases by 10 º and can be calculated with the following equation:

$$Q_{10} = e^{\beta \times 10} \quad \mathbf{(6.2)}$$

where β is determined by fitting equation 6.1 to the data.

The uncertainty of the longer-term methane balances (E) was estimated using a methodology similar to that of Rinne *et al.* (2007). For days when fluxes were measured, daily averages were calculated as the mean of the measured hourly fluxes and the uncertainty was estimated as the standard error of the mean (SE_{obs}). The uncertainty associated with each daily modelled flux was estimated by applying an error term based on the measured versus modelled data fit (E_{mod}). These daily error estimates were then summed using standard error propagation:

$$E = \sqrt{\sum_{i}^{n} (SE_{\mathrm{obs}})^2 + \sum_{i}^{n} (E_{\mathrm{mod}})^2} \qquad \textbf{(6.3)}$$

where, in addition to the terms mentioned above, n is the number of days for which the errors must be calculated.

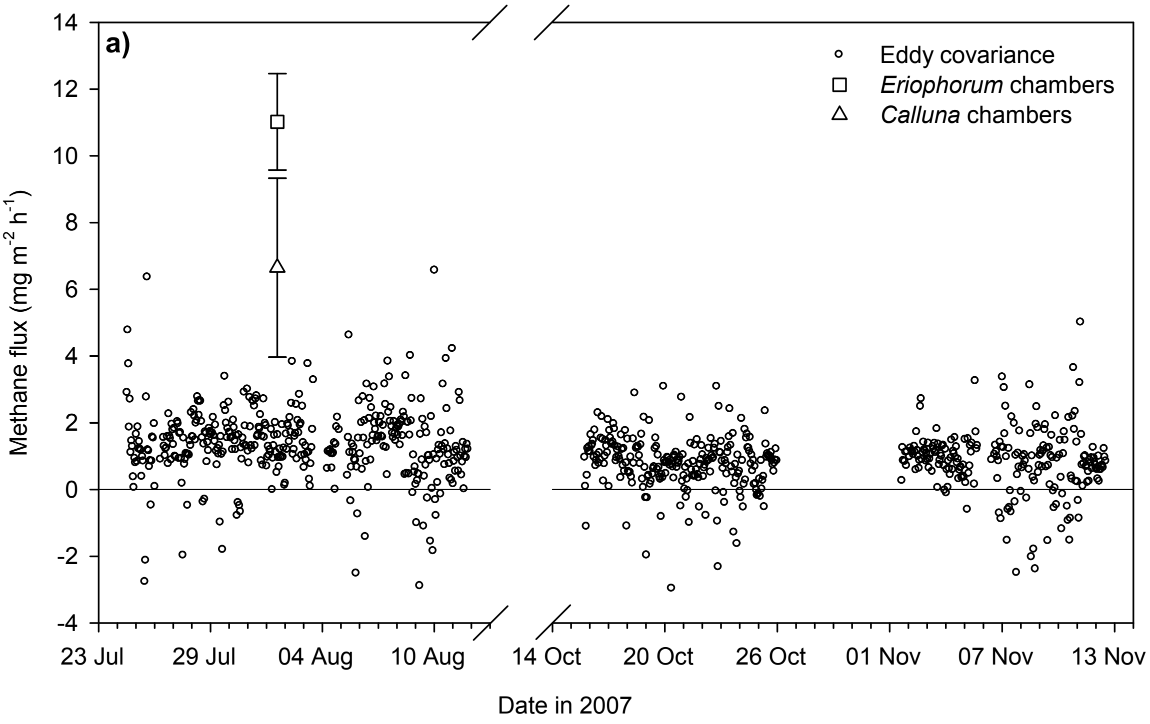
6.2.6 Statistical analysis

Mean differences in the chamber-based methane fluxes from the four vegetation types were compared using non-parametric Kruskal-Wallis analysis of variance (ANOVA), performed using SPSS version 12.0.1 (SPSS Inc, Chicago, Illinois, USA). The Regression Wizard in SigmaPlot 10 (Systat Software, Inc., Chicago, Illinois, USA) was used for regression analysis to determine relationships between environmental variables, fluxes and model residuals and for assessing model fit by plotting measured versus modelled fluxes.

6.3 Results

6.3.1 Temporal variation of methane fluxes

Hourly fluxes were obtained over 42 days during 2007, in campaign mode. Measurements were made in July-August, October and again in November (Figure 6-1). Hourly fluxes were generally positive, showing that the blanket bog at Bog End, Moor House NNR was a source of methane during the measurement periods. A number of hours were recorded as having negative fluxes, apparently exhibiting net methane uptake. A number, but not all of these points were associated with periods of low turbulent mixing and were filtered out utilising a friction velocity filter. Those that remain are believed to be a result of the relatively large uncertainty of individual measurements relative to the low fluxes observed, rather than the product of methanotrophic activity. Hourly fluxes were variable throughout the period, ranging from -2 to +6 mg m^{-2} h^{-1}, but mostly within a range of 1 to 3 mg m^{-2} h^{-1}. Because of the scatter present in the hourly data set, seasonal differences are more obvious in plots of daily fluxes.



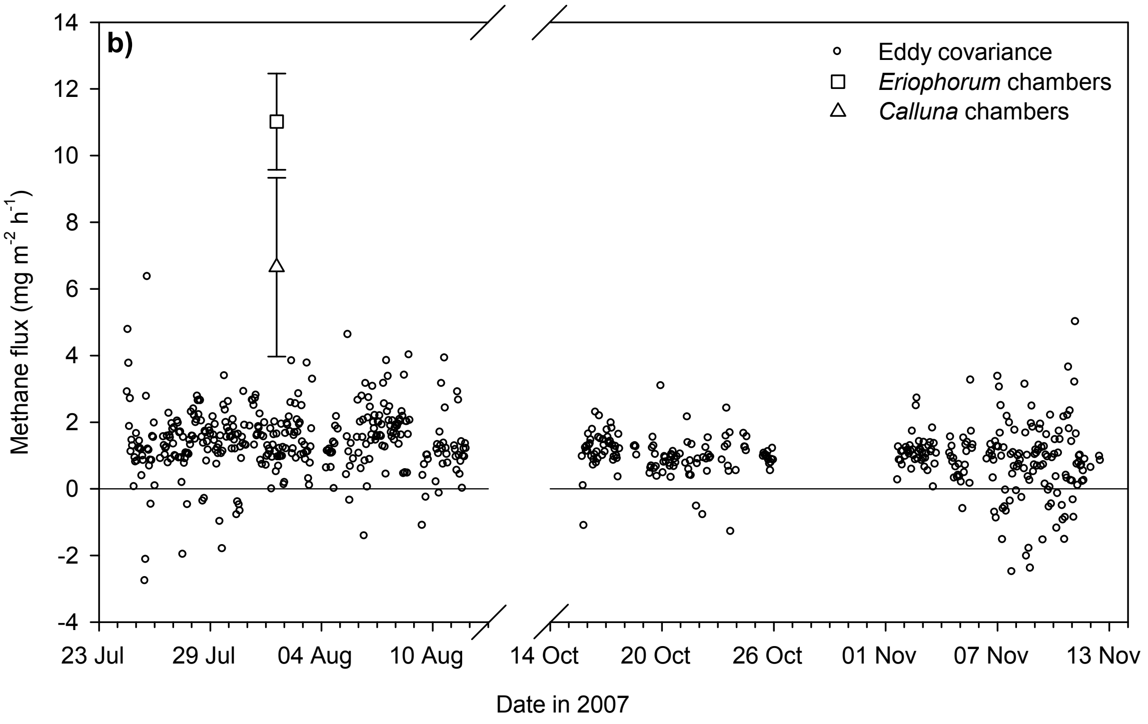


Figure 6-1: Hourly methane fluxes measured using eddy covariance during three campaigns in 2007; a) screened for instrument malfunctions; b) screened for both instrument malfunctions and low turbulent conditions. The mean fluxes ± one standard error from chamber measurements made on 01 August are also shown.

There was some evidence of lower fluxes being measured during periods of low turbulent mixing (Figure 6-2). When hourly fluxes were plotted against friction velocity, there was a tendency for lower fluxes when the friction velocity was calculated as being less than 0.2 m s^{-1} (Figure 6-2a & b). Consequently, these fluxes were excluded from further analysis. This filter excluded 24 % of the 869 available hourly measurements, leaving 655 quality-controlled data points for the remaining analysis (Figure 6-1b). This friction velocity effect on measured methane fluxes was in contrast to the lack of any discernable effect on CO_2 fluxes (Figure 3-7). As the movement of the two gases through the atmosphere will be controlled by the same processes, it is expected that their fluxes will respond similarly to variations in friction velocity. It is speculated that the relatively short measurement period for methane fluxes may have captured specific atmospheric conditions at the site leading to an apparent effect, which was not obvious when examining the larger volume of CO_2 flux data.

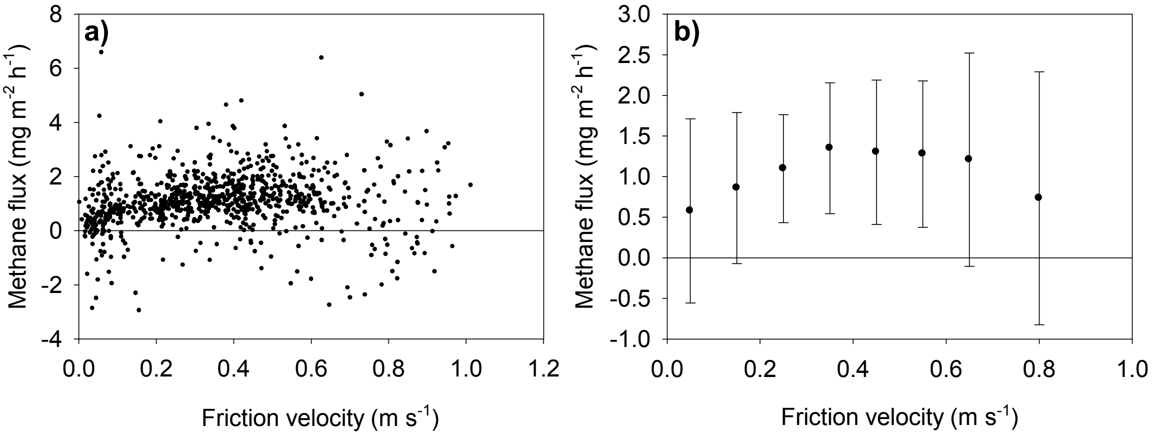


Figure 6-2: Relationship between methane fluxes and friction velocity. a) Points are hourly average fluxes; b) Hourly methane fluxes were binned into eight friction velocity categories, points are mean values ± one standard deviation.

For comparison, the mean fluxes from the closed chamber measurements are plotted on the same graph as the eddy covariance fluxes in Figure 6-1. The mean values from the plots most representative of the eddy covariance flux footprint were similar to, but higher than, the eddy covariance measurements at 6.65 ± 2.68 mg m^{-2} h^{-1} from *Calluna* and 11.02 ± 1.45 mg m^{-2} h^{-1} from *Eriophorum* plots. There was, however, some overlap, with individual measurements varying from a minimum of 1.26 mg m^{-2} h^{-1} to a maximum of 16.41 mg m^{-2} h^{-1}. The mean methane fluxes from the small areas of *Juncus* and wet *Sphagnum* were higher again and are shown in comparison to the *Calluna* and *Eriophorum* fluxes in Figure 6-3. There was however a considerable degree of variation in the fluxes within the individual vegetation types, in what was a relatively small sample size and the mean values were not significantly different ($p > 0.05$).

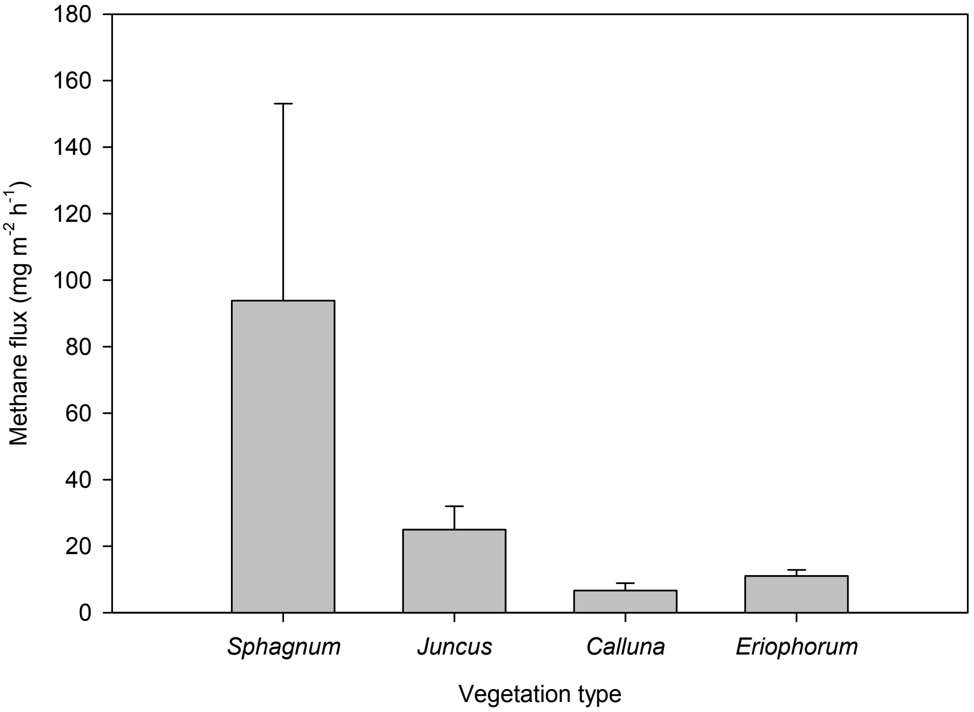


Figure 6-3: Methane fluxes measured at plot scale within the eddy covariance flux footprint using static chambers. Measurements were taken on 01 August 2007 during the first methane eddy covariance measurement campaign. Each bar is the mean + one standard error (*Sphagnum*, $n = 3$; *Juncus*, $n = 3$; *Calluna*, $n = 5$; *Eriophorum*, $n = 5$). Mean values were not significantly different ($\chi^2 = 3.259$; d.f = 3; $p = 0.353$).

The data from days when there was 66 % or better data-coverage were examined for the presence of any diurnal cycle of methane fluxes. Normalised hourly fluxes were created by dividing each hourly flux by the median flux for that day. The mean normalised flux for the whole period was calculated for each hour of the day. There was no evidence of a systematic diurnal variation in fluxes (Figure 6-4). The lack of a diurnal pattern means that daily fluxes can be justifiably calculated as the mean of the available measurements, even if some hourly data are missing. Nevertheless, to reduce the random uncertainty, daily means were only calculated for days when four or more hourly data points were present (39 days were included, with an average of 15 hourly data points each).

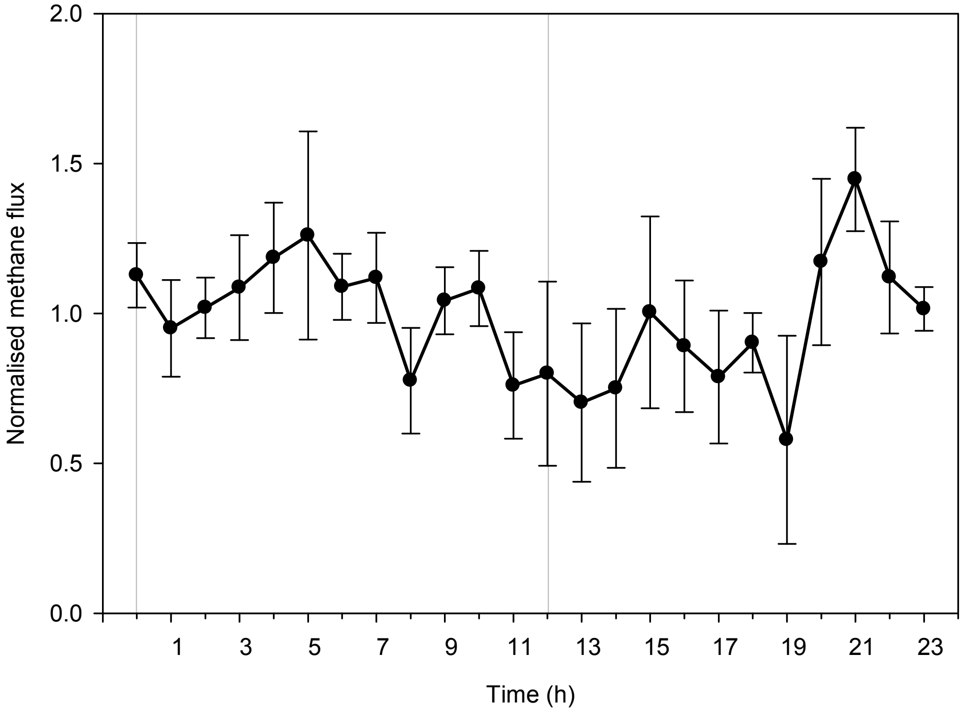


Figure 6-4: Hourly methane fluxes for the measurement period normalised by the daily median flux, only days with over 66 % data coverage were included. Data points are means ± one standard error (*n* varied depending on the availability of quality controlled data but was between 29 and 32.

During the methane flux measurement period, the water table fluctuated between being close to the surface and up to 14 cm below it, closely following the pattern of precipitation (Figure 6-5). The same trend was visible when viewing the soil moisture data. However, the variation was limited with relatively high soil moisture levels throughout the period; the daily mean never dropping below 82 % VWC. Soil temperature measured at 15 cm depth, showed a typical seasonal decline, from highs of over 11 ºC in August to a low of close to 5 ºC at the end of the final campaign in November. There was a degree of variation in daily methane fluxes, but in general, fluxes were highest during the July-August campaign (maximum of 37.34 ± 8.18 mg C m^{-2} d^{-1}) and lowest in November (minimum of 10.21 ± 5.69 mg C m^{-2} d^{-1}). The seasonal trend appeared to follow that of soil temperature.

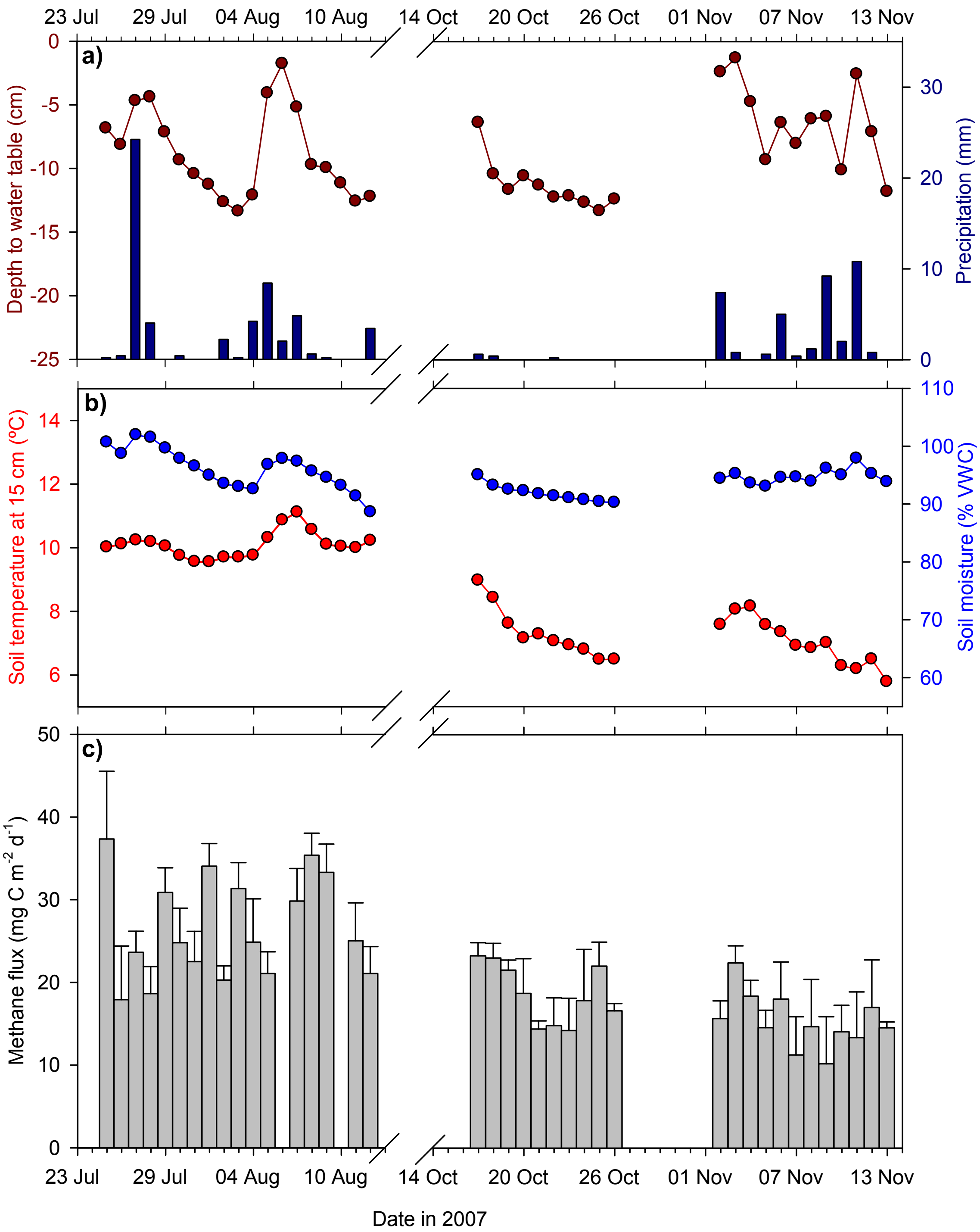


Figure 6-5: Daily methane fluxes and environmental variables at Bog End, Moor House NNR, for the measurement periods in 2007: a) Depth to the water table (cm) and total precipitation (mm); b) Soil temperature at 15 cm depth (ºC) and soil moisture (% VWC) and c) Eddy covariance methane flux (mg C m^{-2} d^{-1}; error bars denote + one standard error of the mean). Except for precipitation, all data are daily means.

6.3.2 Relationships with between methane flux and environmental variables

There was a strong relationship between daily methane fluxes and temperature. The exponential model (Equation 6.1) was fitted to plots of daily methane fluxes against a range of air and soil temperatures (Figures 6-6 and 6-7). Air temperatures were able to explain less than 50 % of the variation on fluxes; improvements came from using soil temperatures. Soil temperature measured at 15 cm, the deepest measurement point, yielded the best relationship and explained over 70 % of the daily flux variation (Figure 6-6).

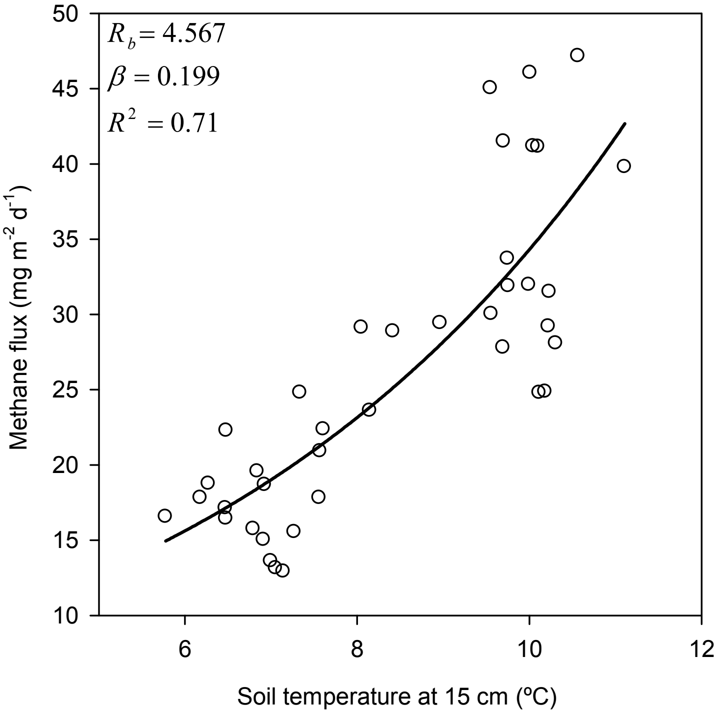


Figure 6-6: Relationship between daily methane flux (mg m^{-2} d^{-1}) and soil temperature (ºC) at 15 cm. The line shows the exponential model fitted to the data: $y = 4.567\ e(0.199x)$.

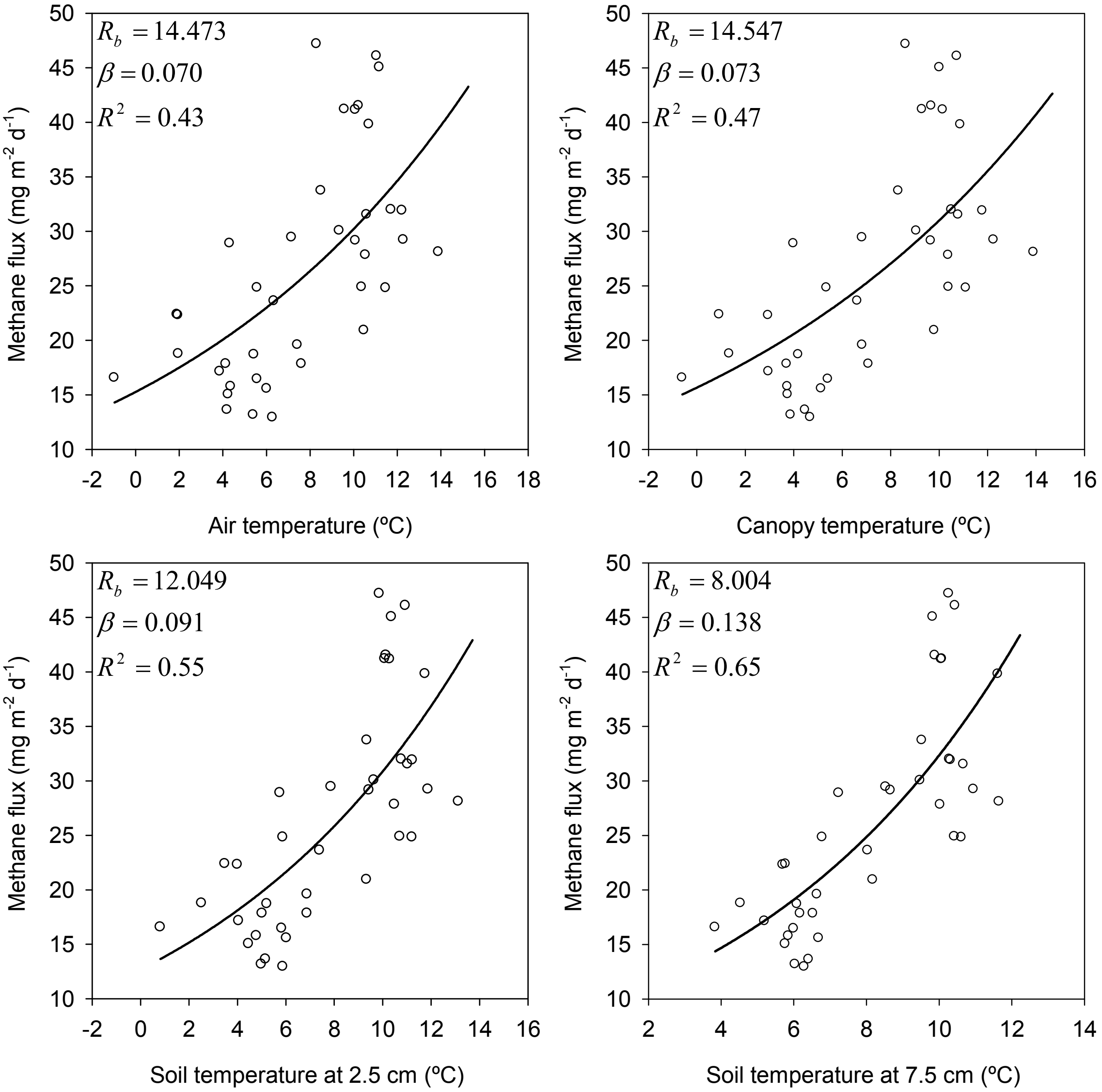


Figure 6-7: Relationships between daily methane flux (mg m^{-2} d^{-1}) and temperature (°C) measured at a range of air, canopy and soil temperatures. Parameters from the fitted relationships are shown.

There was no relationship between daily methane fluxes and the position of the water table (Figure 6-8; $p > 0.05$). There was however, a weak ($R^2 = 0.24$) but significant relationship with the soil moisture content of the peat (Figure 6-9), with daily fluxes tending to be lower when the peat was most saturated. A similar relationship was found with atmospheric pressure, with higher fluxes on days when atmospheric pressure was lowest (data not shown). Both of these apparent relationships were tested further by plotting the residuals of the soil temperature model against atmospheric pressure and soil moisture. In both cases, there was no relationship, suggesting that after the effects of temperature had been removed; neither soil moisture status nor atmospheric pressure played a role in regulating the daily methane flux during the measurement period (Figure 6-10; $p > 0.05$).

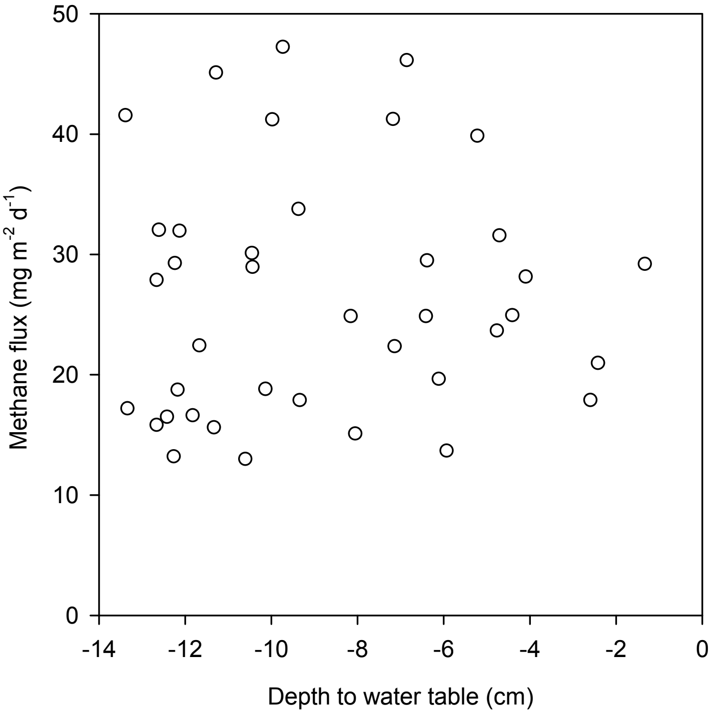


Figure 6-8: Relationship between methane flux (mg m^{-2} d^{-1}) and depth to the water table (cm) ($y = 0.141x + 27.549$; $R^2 = 0.0024$; $p = 0.77$).

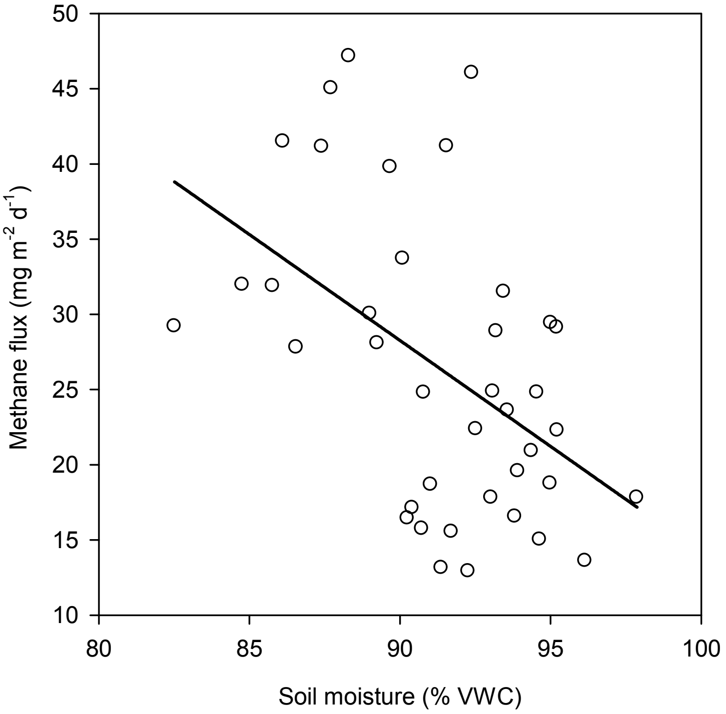


Figure 6-9: Relationship between methane flux (mg m^{-2} d^{-1}) and soil moisture content (%VWC) (y = -1.409x + 155.030; R^2 = 0.24; p < 0.005).

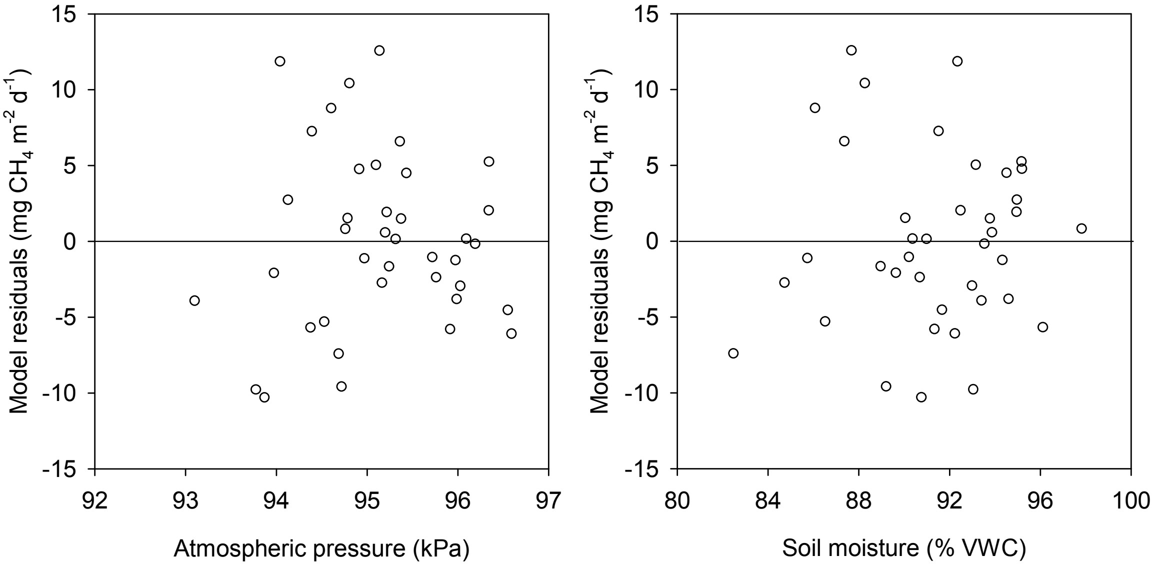


Figure 6-10: Residuals of the temperature model plotted against atmospheric pressure (y = 0.134x -12.823; R^2 = 0.0004; p = 0.906) and soil moisture (y = 0.055x -5.058; R^2 = 0.0011; p = 0.844).

6.3.3 Temperature sensitivity

The temperature sensitivity of the methane flux was calculated based on the flux-temperature relationships shown in Figures 6-6 and 6-7. Air and near-soil-surface temperatures produced Q_{10} estimates of between 2.0 and 2.5 (Table 6-1). When temperatures were measured at increasing depth, the relationships improved to R^2 values of 0.71, but the calculated temperature sensitivity reached values of between 4.95 and 7.32.

Table 6-1: The temperature sensitivity of the methane flux. The Q_{10} function is calculated using different soil temperature depths and air temperature based on the relationships shown in Figures 6-6 and 6-7.

	R^2	Q_{10}
Air temperature	0.43	2.01
Canopy temperature	0.47	2.08
Soil temperature at 2.5 cm	0.55	2.48
Soil temperature at 7.5 cm	0.65	3.97
Soil temperature at 8.0 cm	0.71	4.95
Soil temperature at 15.0 cm	0.71	7.32

6.3.4 Model development

A model of daily methane flux was developed based on a study of the relationships between measured fluxes and environmental variables. The environmental variable that best described the variation in daily methane fluxes during the measurement period was soil temperature at 15 cm depth. A range of other variables were tested and were not found to exhibit any relationship with measured fluxes, so no other variables were incorporated and a purely temperature-dependent model was employed. The performance of the exponential-soil temperature model is presented in Figure 6-10.

The three measurement campaigns took place during the summer and autumn of 2007. Other campaigns planned for winter (February 2008) and spring (April 2008) were not possible due to technical difficulties with the TGA100A methane analyser. The results from those extra two campaigns would have provided coverage of methane fluxes for a greater range seasonal periods and environmental conditions. This data limitation meant that it was not possible to run an annual model without extrapolating out of the range of the measured flux-soil temperature relationship. Because of this, a growing season model was run for the growing season period, when the soil temperature range was within that of the measurement periods, from 22 April to 12 November 2007.

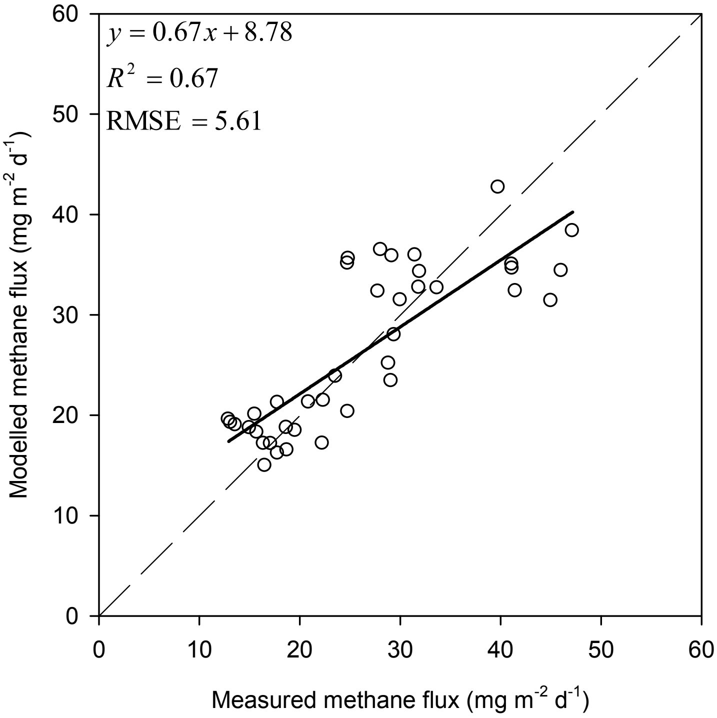


Figure 6-11: Modelled flux versus mean daily methane flux (mg m^{-2} d^{-1}) for the three measurement periods. An exponential model driven by soil temperature measured at 15 cm provided the best fit to the data. Dashed line represents a 1:1 relationship.

6.3.5 Seasonal and annual methane budgets

Based on a combination of measured and modelled fluxes, the Bog End site is estimated to be a net methane source, of 4.35 g C m^{-2}, for the study period of mid April to mid November 2007 (Figure 6-12). The uncertainty around this figure was estimated first for the measured fluxes (39 days) and then for the modelled results (173 days), following the standard error propagation procedure set out in Section 6.2.5. The accumulated error across the study period was 0.09 g C m^{-2}. If the assumption is made that the errors are normally distributed, this figure can be multiplied by 2.58 to yield the 99 % confidence interval of 0.24 g C m^{-2}.

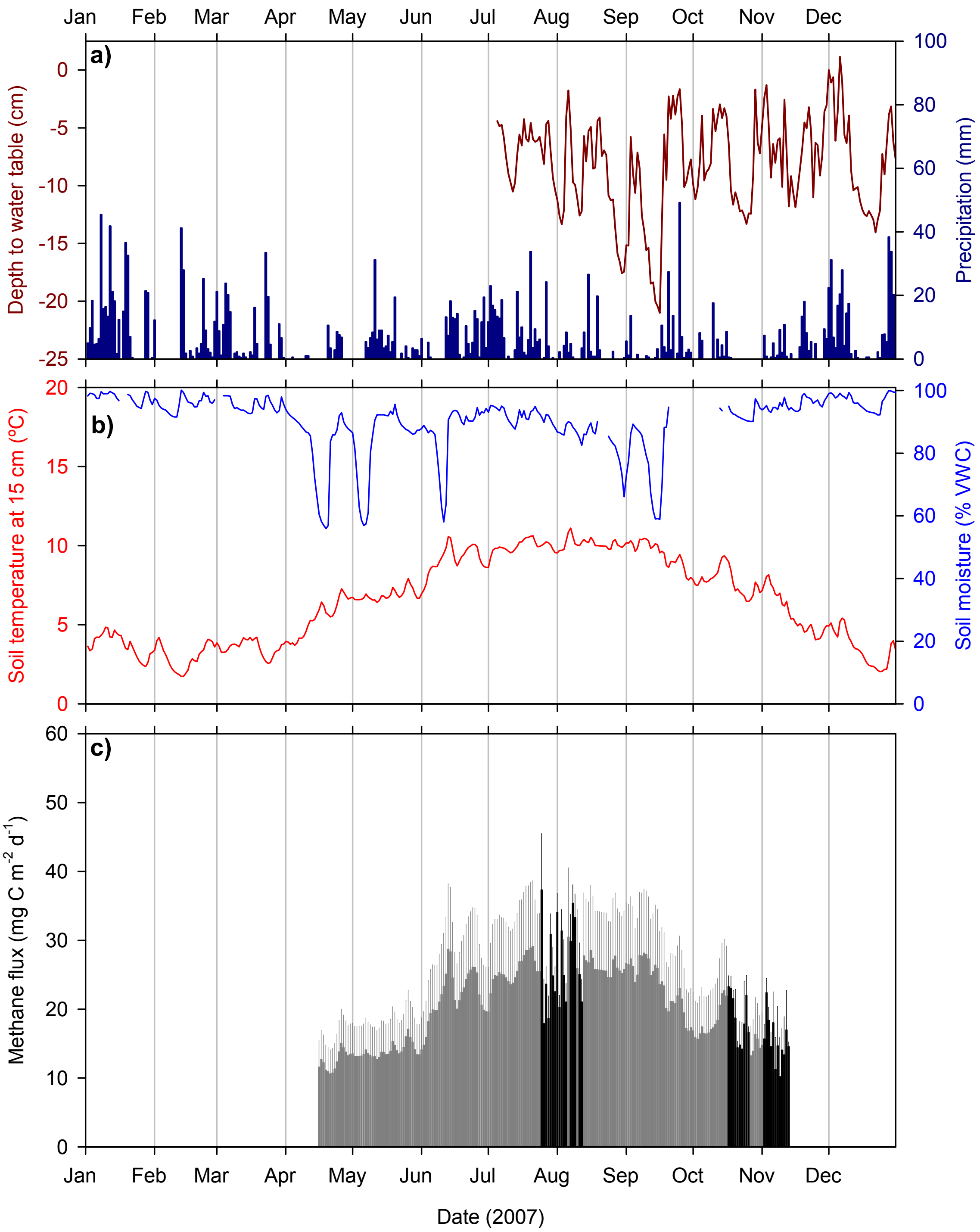


Figure 6-12: Daily methane fluxes and environmental variables at Bog End, Moor House NNR, for 2007: a) Depth to the water table (cm) and total precipitation (mm); b) Soil temperature at 15 cm depth (ºC) and soil moisture (% VWC) and c) Methane flux (mg C m^{-2} d^{-1}), black bars are the daily means (+ one standard error) from hourly measurements during the three measurement campaigns. Grey bars are modelled fluxes (+ error estimate) based on the temperature model.

During the seven month study period, methane fluxes were measured on days with a wide range of mean temperatures, including the warmest and coolest days of the year. The fluxes for the remaining days were modelled based on the soil-temperature relationship and so track the seasonal changes in temperature at the site (Figure 6-12). While measured fluxes were made for the full range of soil temperatures during the study period, the same was not true for several of the other potentially important environmental variables. In particular, the flux measurement campaigns failed to capture the occasional summer-time dry periods. For example, for periods of several days, but often no more than a week, soil moisture levels dropped to less than 60 % VWC and the water table fell to between 15 and 20 cm below the surface.

6.4 Discussion

6.4.1 Spatial and temporal variation of methane fluxes

Studies presenting methane fluxes from blanket bog ecosystems are limited in number (Fowler *et al.*, 1995, Hargreaves and Fowler, 1998, MacDonald *et al.*, 1998, Laine *et al.*, 2007, Ward *et al.*, 2007, McNamara *et al.*, 2008). This study has produced estimates of the hourly flux of methane from the peat soils of a blanket bog to the atmosphere for a period of 42 days during the summer and autumn of 2007. Hourly fluxes showed considerable variation and ranged from between -2 to +6 mg m^{-2} h^{-1}. The negative values are taken as representing the relatively large random uncertainty when measuring low fluxes, rather than being taken as evidence for methane uptake by the soils. Rinne *et al.* (2007), Sachs *et al.* (2008) and Wille *et al.* (2008) all reported a similar phenomena when measuring relatively low methane fluxes with the same instrument. Static chamber measurements from this study (Figure 6-3) and others (Ward *et al.*, 2007, McNamara *et al.*, 2008) have not found any evidence of methanotrophic activity from the blanket bog peat at Moor House. The fluxes reported here are within the range of those found by other researchers using occasional static chamber measurements at Moor House. McNamara *et al.* (2008) reported summer-time fluxes of between 0 and 4 mg m^{-2} h^{-1}, while Ward *et al.* (2007) found that hourly fluxes were close to zero during winter but reached a high of over 3 mg m^{-2} h^{-1} in September. Relatively low mean fluxes of just 0.6 and 0.4 mg m^{-2} h^{-1} were reported from short-term summer-time studies over blanket bog in Caithness, Scotland (Fowler *et al.*, 1995, Beverland *et al.*, 1996).

In this study, temporal variation was more easily viewed when comparing daily fluxes, the highest fluxes of around 40 mg C m^{-2} d^{-1} occurred in July and August, but there was some variation, with fluxes of just 20 mg C m^{-2} d^{-1} also measured at that time. The lowest fluxes of around 10 mg C m^{-2} d^{-1} were measured in November. In an Irish lowland blanket bog, fluxes ranged from 2 mg C m^{-2} d^{-1} during the winter and a summer peak of 40 mg C m^{-2} d^{-1} (Laine *et al.*, 2007). Further figures for comparison are available if boreal and tundra peatlands are considered. Summer-time fluxes were generally higher at a boreal fen in Finland (40 – 75 mg C m^{-2} d^{-1}) (Rinne *et al.*, 2007), while they were similar to those from a Siberian tundra site (15 – 25 mg C m^{-2} d^{-1}) (Sachs *et al.*, 2008, Wille *et al.*, 2008). Significantly higher methane fluxes have been observed from an inundated temperate marsh in Nebraska, USA, where fluxes increased from 30 mg C m^{-2} d^{-1} in early spring to a peak of 488 mg C m^{-2} d^{-1} in late summer (Kim *et al.*, 1998).

There was no evidence of the systematic diurnal variation in methane fluxes that has been observed in some studies, normalised hourly fluxes from the whole measurement period showed no signs of consistently peaking at a certain time of day. This is consistent with recent findings of Rinne *et al.* (2007). Fowler *et al.* (1995) identified a diurnal variation which correlated with variations in soil temperature, while other have attributed diurnal cycles to the presence of certain vegetation types which have been found to play a role in regulating the transport of methane to the atmosphere in a diurnal manner (Armstrong *et al.*, 1996, Whiting and Chanton, 1996). Kim *et al.* (1998) found a diurnal pattern, whereby fluxes were two to four-fold higher during the day than at night, they also found that the diurnal variation was dependent upon the growth stage of the main plant species of the temperate marsh, *Phragmites australis*. At Bog End, methane flux was strongly controlled by soil temperature at the depths of 8 to 15 cm below the surface. At these depths, the diurnal cycle of temperature variation is particularly dampened, so it is not surprising that a clear diurnal flux pattern is not visible. Furthermore, the plant species present are not believed to be associated with diurnal regulation of methane transport to the surface. *Eriophorum vaginatum* certainly plays a role in methane transport, but it is believed to be a passive process, where the aerenchymous tissue acts as a simple conduit, rather than the plant regulating the gas flow through any changes in stomatal aperture (Greenup *et al.*, 2000, Rinne *et al.*, 2007).

A detailed assessment of the spatial variation of methane fluxes across the landscape and vegetation types was not the aim of this study. The primary flux dataset was obtained by the eddy covariance technique, which produced ‘landscape averaged’ fluxes from a wide area of blanket bog (e.g. Hargreaves and Fowler, 1998). Nevertheless, a set of static chamber flux measurements were made alongside the micrometeorological measurements in order to confirm that the two methods yielded similar results. Fluxes from the chambers were on average higher than those from the flux tower, but there was considerable variation among the small sample size of chamber plots that were measured. The mean values were of the same order of magnitude and there was some overlap of individual measurements. Chamber measurements were taken within four different vegetation types that compose the blanket bog at Bog End, these were *Calluna* and *Eriophorum*, which represent the majority of the area and wet *Sphagnum* and *Juncus*, which although covering very small areas, were included as possible 'hot-spot' sites of methane production. Fluxes were on average higher from the wet Sphagnum and Juncus plots, but the differences were not significant and a larger, more specific study would be required to further test these findings. Other work at Moor House, suggests that methane fluxes should differ significantly with vegetation type. McNamara *et al.* (2008) found higher fluxes were found from 'gully' areas (similar to the wet *Sphagnum* and *Juncus* plots in this study) than from the dominant *Calluna* areas. The highest fluxes were from *Eriophorum* plots in gully locations, where the wet conditions and aerenchymous vegetation combined to promote significant methane release.

6.4.2 Environmental controls on methane flux

Soil temperature at depths of over 8 cm provided the best relationships with daily methane fluxes at the site, suggesting that soil temperature played the most important role in regulating the variation in daily fluxes over the measurement period. A simple exponential model with soil temperature at 15 cm depth provided a good fit to the data. This finding is common to many but not all other studies of methane fluxes at similar peatland sites (Moore and Dalva, 1993, Fowler *et al.*, 1995, Hargreaves and Fowler, 1998, Laine *et al.*, 2007, Rinne *et al.*, 2007). Soil temperature measured deeper in the peat produced the better relationships than temperatures measured at shallower depths. This is the opposite of the situation for the soil CO_2 flux, but consistent with the deeper and more anaerobic soils being the expected location for methane production (Blodau, 2002). The best soil temperature-methane flux relationships produced relatively high temperature sensitivities, with Q_{10} estimates of the order of 5 to 7. However, these high values have been found in other studies (Q_{10} = 1.7 – 16) and there is evidence that the flux of methane is more sensitive to temperature than the flux of soil CO_2 (Dunfield *et al.*, 1993, Walter and Heimann, 2000).

Depth to the water table was unrelated to methane flux and an apparent relationship with soil moisture status disappeared after the variations associated with soil temperature were removed. The absence of any soil moisture or water table effect may well be due to the fact that during the measurement periods, the peat was constantly close to saturation (over 80 % VWC) and the water table did not fall below 14 cm from the surface. Longer-term monitoring 2006 – 2008 suggests that these conditions are typical for most the year at Bog End, but there have been short periods during the summer months when soil moisture fell to close to 40 % VWC and the depth to the water table fell below 20 cm. It is possible that under such conditions, soil moisture or depth to the water table begin to have a significant effect on the methane flux. Other studies have failed to find significant relationships with water table, which they have attributed to a lack of variation in the level of the water table or the maintenance of constantly water-logged conditions (Shannon *et al.*, 1996, Hargreaves *et al.*, 2001, Rinne *et al.*, 2007, Sachs *et al.*, 2008). A number of studies have found significant water table effects, including Bubier *et al.* (2005), comparing methane fluxes between a dry and a wet year. Several other eddy covariance studies have developed relationships between water table depth and temporal variation of fluxes, but these were short-term experiments and relationships were based upon linking fluxes from certain sectors of the flux footprint to the differing water tables in those sectors; in essence using spatial variation to predict temporal variation (Fowler *et al.*, 1995, Hargreaves and Fowler, 1998).

One possibility explaining the difficulty in identifying expected links between water table and fluxes, is that there may be considerable time lags between the change in water table and the observed change in flux magnitude (Moore and Dalva, 1993, Suyker *et al.*, 1996). Changes in methane production in response to changes in the environmental conditions will be in part as a result of changes in the size and activity of the population of methanogenic microbes (Dise *et al.*, 1993). If the microbial populations take time to respond to newly optimum or newly unsuitable conditions, there may be a hysteresis which would make correlating the two factors more difficult (Lloyd *et al.*, 1998). While the role of the water table in controlling temporal variation of methane fluxes may be complex and be highly dependent upon the site-specific conditions, there is agreement that it plays a significant role in controlling the spatial variation of fluxes within a peatland (Moore and Knowles, 1989, Saarnio *et al.*, 1997, Laine *et al.*, 2007).

Sachs *et al.* (2008) found that soil temperature was a relatively small factor in explaining the methane flux at their tundra site. They suggested that the measured flux was primarily controlled by factors affecting methane transport rather than those factors affecting methane production. They found that near-surface turbulence and atmospheric pressure explained 60 % of the flux variation, while soil temperature explained only 8 %. Fluxes were higher on days with high atmospheric turbulence and low atmospheric pressure, the authors hypothesise that these conditions promoted increased methane release from the large inundated areas via increased ebullition. They argue that near-surface turbulence could release bubbles of methane from surfaces below the water table (e.g. Hargreaves *et al.*, 2001), while lower atmospheric pressure may release free-phase gas and result in increased ebullition (Sachs *et al.*, 2008). These processes are less likely to be important at Moor House, where the water table is rarely above the surface and ebullition is unlikely to be a significant methane release pathway.

6.4.3 Seasonal and annual methane budgets

This study has provided a methane budget for the growing season at Bog End, Moor House NNR of 4.35 ± 0.09 g C m^{-2}. This estimate was based on data collected during three measurement campaigns and an associated modelling study. It was originally intended to run further measurement campaigns in order to capture a more complete representation of the seasonal variation of environmental parameters, but this was not possible due to technical difficulties. Because of this, the data were not available to justify modelling the fluxes for a complete annual cycle. One cautionary note concerns the lack data collected during the occasional summer dry periods. Water table depth was not an important factor during the measurement periods and so was not included in the flux model which was used to estimate the seasonal flux. If water table or soil moisture becomes an important factor during those dry periods, those potential effects would not be included in the modelled fluxes. If there was a water table effect, whereby fluxes were suppressed during summer dry periods, then the results from the temperature model would overestimate the methane flux during these periods. At present this is merely a hypothesis and further data collection during those conditions would be required to determine if such a process occurs at the site.

Results from other sites suggest that winter-time fluxes would make a small but significant positive contribution to the annual figure (Laine *et al.*, 2007, Rinne *et al.*, 2007, Ward *et al.*, 2007). Therefore, the annual figure is likely to slightly higher than the seasonal estimate quoted above. Considering that point, the seasonal figure compares well with the only other available estimates for annual methane fluxes over blanket bog in the British Isles of 4.5 g C m^{-2} yr^{-1} at an Irish lowland blanket bog (Laine *et al.*, 2007) and 5.16 g C m^{-2} yr^{-1} at a blanket bog in Caithness, Scotland (Hargreaves and Fowler, 1998). These are greater than the estimate from a Siberian tundra site of just 2.3 g C m^{-2} yr^{-1} but lower than those measured at a boreal fen in Finland of 9.45 g C m^{-2} yr^{-1}. This study has shown that the flux of methane is an important component of the carbon balance at this blanket bog and that further work is warranted at such sites to reduce the uncertainty and quantify the role of summer dry periods and winter season fluxes.

6.5 Summary

Methane flux measurements over blanket bog ecosystems remain relatively uncommon; this study produced hourly and daily estimates of the methane flux for a UK peatland. Summer time fluxes were similar to those found at an Irish blanket bog, but generally lower than those measured at a boreal fen.

Closed chamber flux measurements showed that the ‘landscape averaged’ fluxes measured by the eddy covariance method were the sum of highly variable fluxes from individual components and vegetation patches within the flux footprint.

When hourly fluxes were examined, there was no evidence of any systematic pattern of diurnal variation in the magnitude of the methane emissions.

Soil temperature measured at a depth of 15 cm best explained the variation of daily methane fluxes. The relationship was stronger than those with temperatures measured at shallower depths, which is consistent with deeper peats being the site of methane production. Both water table and soil moisture were consistently high during the measurement periods and neither factor was able to explain any of the variation in methane fluxes.

A simple model based on a relationship with soil temperature was used to estimate daily fluxes for the remainder of the growing season and produce a seasonal estimate of the total amount of methane emitted.

For the period of mid-April to mid-November 2007, the blanket bog at Bog End, Moor House was a source of methane, with an estimated 4.35 ± 0.09 g C m^{-2} lost from the peat to the atmosphere.

CHAPTER 7

GENERAL DISCUSSION AND SYNTHESIS

7.1 Introduction

This final chapter aims to draw together the findings from the previous four data chapters, to relate some the major findings to the published literature and suggest some aspects that might be pursued as future research. The broad, overarching theme to this work was to provide improved understanding of the carbon balance of an area of upland blanket bog in the north Pennines. All of the major pathways of gaseous carbon flux were measured at a field site at Moor House NNR. A variety of different techniques were employed but the emphasis was on generating high temporal resolution datasets of carbon fluxes over time periods of months and seasons where possible, or ‘campaign’ measurements where necessary. These datasets were used to explore relationships between variations in fluxes and environmental variables. This enabled the determination of which factors were important for controlling the flux or carbon and an assessment of whether the controlling factors differed for the various flux pathways. Once such relationships were established, a final aspect of the work was to utilise these parameters to model the fluxes for periods when data were not available. These exercises generate important outputs, such as: how much carbon is being cycled over longer term periods of days, months, seasons and years?

Chapter 3 presents a half-hourly net CO_2 flux dataset which was collected and gap-filled for a period of 22 months. The net CO_2 budget was estimated for the whole period and an annual cycle. A flux partitioning model allowed an estimate for the relative roles of the component fluxes of gross primary productivity and ecosystem respiration.

Chapter 4 described the development of a new methodology for making accurate measurements of soil CO_2 fluxes, by combining a high performance automated chamber system with surface measurement collars. The results suggested that the standard technique of inserting measurement collars deep into the soil can significantly affect fluxes.

In Chapter 5, the focus remained with the flux of soil CO_2. Hourly fluxes were measured over a period of just over seven months and the relationship of fluxes with temperature and soil moisture enabled the estimation of seasonal and annual fluxes.

Finally, in Chapter 6, the work focussed on quantifying the magnitude and controlling variables of the flux of methane from the peat to the atmosphere. The site was found to be a source of methane and an estimate of the seasonal flux was made.

7.2 Measured components of the carbon cycle

The annual carbon fluxes as estimated by the work reported in this thesis are presented together in Figure 7-1. With the exception of the methane flux, the figures cover the period of July 2006 to July 2007; the figure for methane is a seven month growing season estimate from the 2007 calendar year. The high net CO_2 flux was the balance of relatively high primary productivity and ecosystem respiration fluxes. An estimated 20 % of the carbon fixed during photosynthesis was not respired back to the atmosphere, but was either stored within the vegetation and soils or alternatively lost from the system via another flux pathway.

The application of soil CO_2 flux chambers together with the eddy covariance system allowed the rare opportunity of further partitioning the net CO_2 flux. An estimate of ecosystem respiration existed as a result of the flux partitioning routine, when annual soil respiration (R_s) is subtracted from ER; the remaining flux must the result of above-ground plant respiration (R_a). Above-ground plant respiration made a larger contribution to ecosystem respiration than did soil respiration; the ratio of R_a to R_s was 64:34. Soil respiration accounted for approximately 30 % of the carbon fixed during photosynthesis. Although without further experimentation, it is not possible to say what proportion of carbon respired from the soils was recently fixed and what proportion resulted from the break down of older carbon stocks within the peat. There has been some work reported in the literature which has aimed to quantify the age and source of the carbon that is respired. Stable isotopes and analysis of the radiocarbon signature of respired CO_2 have proved useful in determining that the flux of respired carbon may originate from a range of sources and be composed of both recently assimilated carbon and the product of the decomposition of older carbon stocks (Dioumaeva *et al.*, 2002, Bahn *et al.*, 2009).

The seven month estimate of total methane flux represented just 2.5 % of the annual NEE. The additional small methane flux that is expected from the winter months, would increase this percentage slightly. Even considering the extra winter flux, the methane is likely to make a relatively small contribution to offsetting the carbon gains of NEE, compared to other sites. Figures of 22 % (Rinne *et al.*, 2007), 5.6 % (Laine *et al.*, 2007), 4.2 % (Cao *et al.*, 1996) and have been reported by other studies. The study of Rinne *et al.* (2007) in particular shows that the flux of methane can be significantly more important to the overall carbon budget in certain ecosystems, such as a boreal fen.

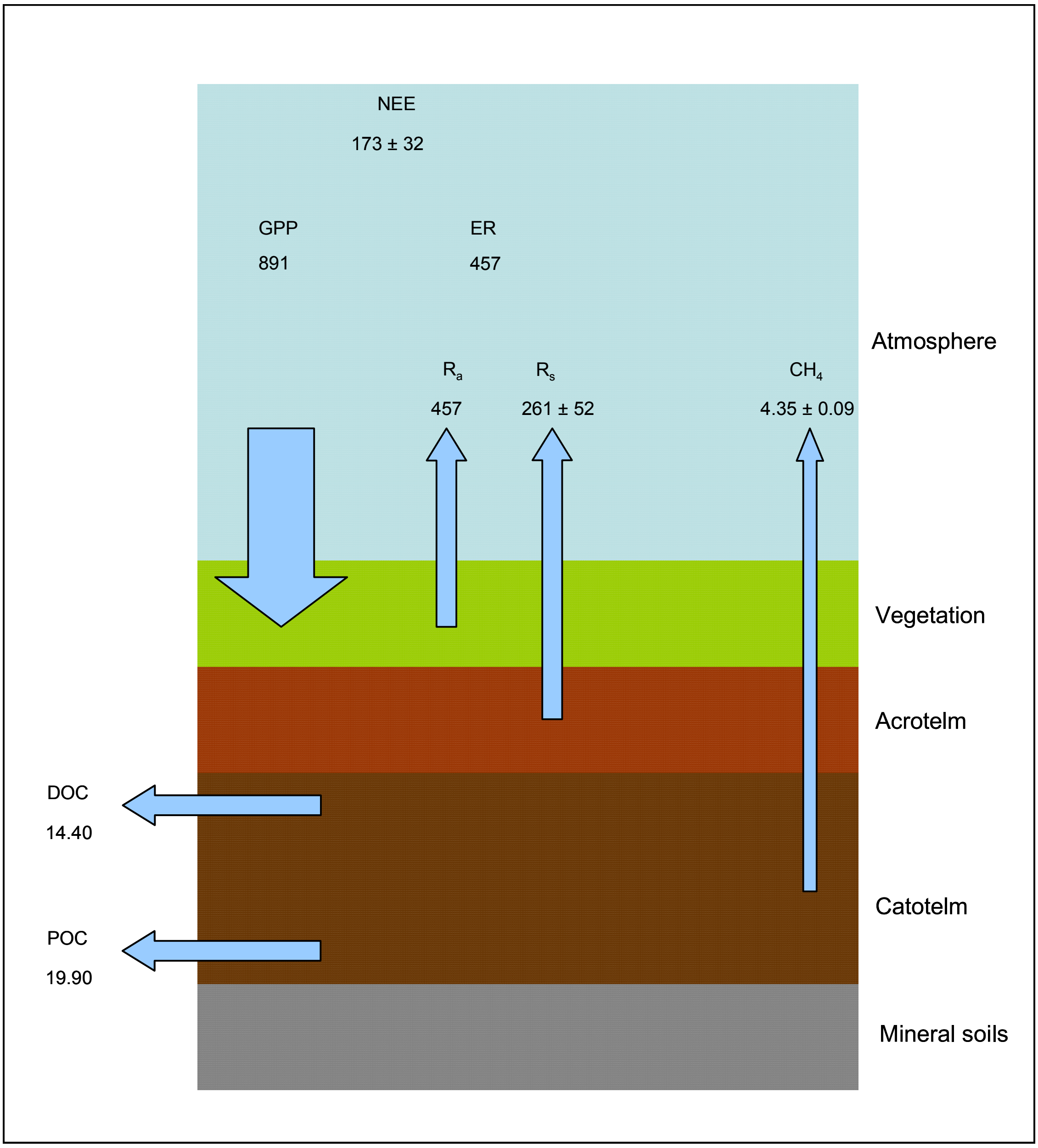


Figure 7-1: A schematic representation of the carbon fluxes at Bog End, Moor House showing the estimates of the magnitude of the measured and modelled fluxes (g C m^{-2} yr^{-1}) from this study (Error estimates are shown where available). To complete the carbon budget, estimates of the amount of carbon lost as DOC and POC are taken from Worrall *et al.* (2007).

7.3 Factors controlling the flux of carbon

Most studies of carbon fluxes within peatlands have found that the seasonal and annual variations in the magnitudes of the carbon fluxes considered in this thesis are controlled by temperature and soil moisture or water table level. Many studies have reported differing relative roles for the two driving variables (Moore and Knowles, 1989, Moore and Dalva, 1993, Blodau and Moore, 2003, Lafleur *et al.*, 2005). At this blanket bog site, variations in temperature were found to be the most important factor in explaining variations in the magnitude of the measured fluxes. The flux of methane was closely related to soil temperature at a depth of 15 cm and there were no relationships with soil moisture or water table depth. Ecosystem respiration was similarly controlled by variations in air and near surface soil temperature. There was however, evidence of a soil moisture effect on soil CO_2 fluxes, although this was not evident in the larger ecosystem respiration flux, of which it is a component. A purely temperature driven model under-predicted soil CO_2 fluxes during dry summer spells, the incorporation of soil moisture into the model, improved the fit. It is suggested that under normal circumstances, soil moisture level is unimportant because the peat is almost constantly close to saturation anyway, but when the peat begins to dry out, then variations in the level of soil moisture become an important controlling variable alongside temperature. Lafleur *et al.* (2005) showed that ecosystem respiration can be explained by temperature and be independent of water table depth when a peatland is close to being constantly saturated.

The methane measurement campaigns were unable to capture methane fluxes during the occasional summer dry spells, and this may explain the lack of a water table effect in this study (Bubier *et al.*, 2005). Temperature was the important driving variable, but before any role for water table depth is excluded, measurements are required from those times of the year when the water table drops to 20 cm below the surface.

This study has reported that all of the key fluxes that are important in determining the size of the carbon sink of an area of blanket bog are driven by variations in temperature, there was also evidence that dry conditions in the summer promotes larger losses of carbon through an increased soil CO_2 flux. The most recent climate change projections predict summer temperature increases of around 3ºC and a reduction in summer rainfall of between 20 to 30 % for the UK (50% probability level by 2080 under a medium emissions scenario) (Murphy *et al.*, 2009). Under a trend towards these conditions, an increase in carbon lost to the atmosphere is anticipated as a result of warmer summer temperatures and a likely increase in the frequency of summer dry periods when water table depth and soil moisture levels drop. The response of the small methane flux is likely to be complex and dependent upon whether it is significantly reduced by summer dry periods. Understanding the capacity of the vegetation to maintain high carbon sequestration rates during increasingly frequent periods of hot summer drought may be key to determining how the overall carbon budget presented here will change under a changing climate.

7.4 Towards a complete carbon budget

Landscape or catchment scale carbon budgets that consider all of the main pathways by which quantities of carbon move into and out of a system remain relatively rare. Worrall and colleagues have produced a number of estimates for the Trout Beck catchment at Moor House as more data about the individual pathways has become available over recent years (Worrall *et al.*, 2003, Worrall *et al.*, 2007b, Worrall *et al.*, 2009). Budgets are available for several other sites that include most, but not all, of the important carbon pathways; Billet *et al.* (2004) measured the net CO_2 fluxes as well as the major fluvial fluxes, but did not quantify methane emissions at their site. At an Irish lowland blanket bog, both the net CO_2 (Sottocornola and Kiely, 2005, Laine *et al.*, 2006) and methane fluxes (Laine *et al.*, 2007) have been measured but no estimates of the carbon losses as fluvial fluxes exist. The work of Worrall and colleagues includes estimates of carbon inputs as rainfall dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) and fluvial fluxes of DOC, particulate organic carbon (POC) and dissolved CO_2 (Worrall *et al.*, 2003, Worrall *et al.*, 2007b). Their most recent budget includes modelled primary production and soil respiration but a limited set of field measurements were used to calibrate the models (Worrall *et al.*, 2009). Finally, methane emissions were not measured at the site but were estimated from general relationships from the literature between methane flux and depth to the water table (Worrall *et al.*, 2009). Worrall *et al.*'s (2007b) estimates were combined with the annual estimate of the net CO_2 flux from this study in Chapter 3. Those calculations revealed that the net carbon gain of 173 ± 32 g C m^{-2} yr^{-1} through net CO_2 exchange was offset by a net loss of 38.44 g C m^{-2} yr^{-1} from the other flux pathways which resulted in a revised figure of 134.56 ± 32 g C m^{-2} yr^{-1}. The net offset figure included the estimate of methane emissions from literature relationships of 3.88 g C m^{-2} yr^{-1}, the work presented in Chapter 6 allows this figure to replaced with one based on actual measurements at Moor House, 4.35 ± 0.09 g C m^{-2} yr^{-1}. This later figure was a seasonal estimate for the seven months of the year when methane emissions are expected to be at their highest. Some additional small contribution to the estimate is expected from the fluxes during the winter months. The field based estimate is similar to the original figure proposed by Worrall *et al.* (2007b) and makes only a very small change to the overall carbon budget, especially considering the relatively small size of the flux and the uncertainty estimates of the other larger fluxes. Nevertheless, an estimate of methane emissions based on field measurements from the site was required to add credence to the overall carbon budget for the site of 134.09 ± 32 g C m^{-2} yr^{-1}. This figure represents a relatively high carbon sink to other studies, for the same site Worrall *et al.* (2009) arrived at a figure of between 20 and 91 g C m^{-2} yr^{-1}. They used the same estimates for many of the pathways as this study, but the difference was largely due to their lower estimate of the net CO_2 flux. Billett *et al.* (2004) found that a lowland peatland catchment in Scotland was either a carbon source or carbon neutral, with fluvial carbon losses measured as being greater than or equal to the net CO_2 flux.

7.5 The carbon balance of the north Pennines

The North Pennines Area of Outstanding Natural Beauty has estimated that there are 900 km^2 of ‘peatlands’ within their area of operation (Leadbitter, pers com), which includes most of the north Pennines. Considerable caution is necessary when it comes to simply scaling up fluxes measured over a relatively small area to larger parts of the country. But, while heeding such cautions, it is an interesting exercise. If the blanket bog studied at Moor House were typical of the peatlands within the north Pennines, and employing the upper and lower error estimates of the above budget, then they would represent a sink of between 121 and 92 Gg of carbon in a single year. To put these figures into context, they are between 0.06 - 0.10 % of a recent estimate of the total UK fossil fuel emissions of 150.26 Tg C yr^{-1} (Baggott *et al.*, 2005). Some of the reasons why the relatively high carbon uptake reported for Moor House may not be applicable to the rest of the peatlands within the north Pennines are discussed in the following section.

7.6 Further work

There are some obvious avenues for fruitful and necessary further work based on the findings presented in this thesis. Of note are the novel findings relating to collar insertion significantly affecting chamber measurements of soil CO_2 flux that were described in Chapter Four. Further work is warranted to investigate how widespread these effects are when measuring fluxes in different ecosystems. Similar findings to those from this study have already been replicated in experiments in an agricultural grassland and a Lodgepole pine plantation and the results from all three experiments are in preparation for submission (Heinemeyer *et al.*, unpublished data).

The data collection periods were necessarily short because of demands on equipment and the limited time available to a PhD project. A number of long-term monitoring studies have reported considerable interannual variation of the ecosystem level carbon fluxes (Whalen and Reeburgh, 1992, Joiner *et al.*, 1999, Lafleur *et al.*, 2003, Rennermalm *et al.*, 2005). A raised bog can be a considerable CO_2 sink in one year and a more modest one in the next (Sottocornola, 2007). Other interannual studies have shown that peatland ecosystems can come close to switching from a net sink to a net source over two consecutive annual cycles (Aurela *et al.*, 2004). High temporal resolution (half-hourly or hourly) datasets of net CO_2 exchange, soil CO_2 fluxes and methane emissions were produced as a result of this study and measurements were made over a wide range of environmental, climatic and seasonal conditions. This allowed the development of relationships, so that the variation of the various carbon fluxes could be described by variations in the environmental conditions. The parameters derived from these relationships can form the basis for modelling studies to predict fluxes over the longer-term and inform about potential interannual variations. But a note of caution is advised, significant interannual variation in fluxes will likely be a result of unusual conditions, a summer drought for example. Simple empirical models may not be able to correctly represent the fluxes under such conditions. Furthermore, depending on the conditions, an environmental driver might be key to explaining the variation in fluxes in one year but unimportant in the next year. For example, fluctuations in the water table can be important in a dry year but play little role when conditions are generally wetter in another year (Bubier *et al.*, 2005). In this study for example, conditions were generally very wet with high water tables and soil moisture levels prevailing during the measurement period and these factors were generally found to be unimportant in controlling the flux of methane. Longer-term monitoring of the water table at Moor House shows that drier conditions have been recorded (Evans *et al.*, 1999) and the role of water table depth in controlling methane fluxes at the site under such conditions is not known.

There was an indication of potential interannual variation in the magnitude of the net CO_2 flux within this study; while two full years could not be compared, after nine months of the annual cycle, net CO_2 uptake was 60 % higher in year two (July 2007 to April 2008) than it had been in year one (July 2006 to April 2007). Longer-term monitoring would allow a better estimation of interannual variation and increase the likelihood of measuring fluxes during unusual but potentially important events such as summer dry periods.

This study has found that a UK upland blanket bog can be a large carbon sink. But it is important to note that while the site at Moor House is typical of large areas of the upland peats found in the UK in terms of vegetation and soil classification, there are differences which are likely to be significant in terms of the carbon balance. Moor House is a National Nature Reserve and is managed as such. The area at Bog End has not been drained, has not been burnt for at least 60 years and the levels of grazing by sheep are extremely low (Garnett *et al.*, 2000, Worrall *et al.*, 2007a). This is in stark contrast to the majority of blanket bog, certainly in northern England, where draining, burning and grazing have been important management strategies (Ramchunder *et al.*, 2009). Management practices have been shown to alter the carbon balance of blanket bog but these results are from small plot-scale experiments (Ward *et al.*, 2007, Clay *et al.*, 2009). A comprehensive assessment of the carbon budget from a more typical, intensively managed raised bog is currently lacking. The significant carbon sink found at Moor House, will likely represent the optimum conditions for carbon sequestration in what is close to a ‘pristine’ UK blanket bog.

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Appendix 1 – EdiRe processing list used to calculate fluxes at Bog End

The EdiRe software package was used for automatically processing raw data and calculating fluxes of CO_2, methane, sensible and latent heat fluxes. The program was developed by Dr Robert Clement and Prof. John Moncrieff at the University of Edinburgh and is freely available to download at:

http://www.geos.ed.ac.uk/abs/research/micromet/EdiRe/.

A processing list is created, where the relevant procedures, calculations and corrections are applied in the correct order. Various site and instrument specific parameters are also entered. Briefly, operations included:-

- Extraction of raw data from hourly 10 Hz data files
- Filter out raw data based on the CSAT's diagnostic signal
- Despiking of raw data
- Calculate wind direction
- Perform a planar fit rotation
- Calculate and remove the lag between the closed path methane sensor and sonic anemometer
- Calculate means and standard deviations for raw data
- Calculate friction velocity u*
- Calculate initial momentum, sensible heat, latent heat, CO_2 and methane fluxes
- Calculate and apply frequency response corrections to all fluxes
- Calculate and apply Webb corrections to latent heat and CO_2 fluxes

The complete processing list used for calculating eddy covariance fluxes at Bog End is detailed below:

```
Location Output Files
        Output File Calculations =  C:\
        Output File Spectral =
        Output File Wavelet =
        Output File Cross Correlation =
        Output File Distribution =
        Output File Quadrant =
        Output File Reference =
Set Values
        From Time =
        To Time =
        Number of Variables = 6
        Storage Label = Ht
        Assignment value = 3.0
        Storage Label = ZeroPlane
        Assignment value = 0.28
        Storage Label = SampleFreq
        Assignment value = 10
        Storage Label =
        Assignment value =
        Storage Label =
        Assignment value =
        Storage Label =
        Assignment value =
Extract
        From Time =
        To Time =
        Channel = 4
        Label for Signal = U
Extract
        From Time =
        To Time =
        Channel = 5
        Label for Signal = V
Extract
        From Time =
        To Time =
        Channel = 6
        Label for Signal = W
Extract
        From Time =
        To Time =
        Channel = 7
        Label for Signal = C
Extract
        From Time =
        To Time =
        Channel = 8
        Label for Signal = Q
```

```
Extract
        From Time =
        To Time =
        Channel = 8
        Label for Signal = Qc
Extract
        From Time =
        To Time =
        Channel = 9
        Label for Signal = Ts
Extract
        From Time =
        To Time =
        Channel = 10
        Label for Signal = P
Extract
        From Time =
        To Time =
        Channel = 11
        Label for Signal = Diag
Extract
        From Time =
        To Time =
        Channel = 12
        Label for Signal = M
Extract
        From Time =
        To Time =
        Channel = 13
        Label for Signal = Ta
Extract
        From Time =
        To Time =
        Channel = 14
        Label for Signal = E
Linear
        From Time =
        To Time =
        Signal = Qc
        1st Offset = 0
        1st Gain = 55.55556
        1st Curvature = 0
        2nd Offset = 0
        2nd Gain = 1
        2nd Curvature = 0
2 chn statistics
        From Time =
        To Time =
        Signal = W
        Signal = C
```

```
        Storage Label Covariance =
        Storage Label Correlation =
        Storage Label Flux = Fc_before
        Flux coefficient = 1
Raw Subset
        From Time =
        To Time =
        Subset start time(s) = 0
        Subset length(s) = 1800
        Signal for condition = Diag
        Condition operators = <
        Condition (lower limit) = 1
        Condition upper limit =
        Storage Label % removed = PctRemovedDiag
        Number of signals = 12
        Signal Subset = U
        Signal Subset = V
        Signal Subset = W
        Signal Subset = C
        Signal Subset = Q
        Signal Subset = Qc
        Signal Subset = Ts
        Signal Subset = P
        Signal Subset = Diag
        Signal Subset = M
        Signal Subset = Ta
        Signal Subset = E
Skip Next
        From Time =
        To Time =
        Skip conditional variable = PctRemovedDiag
        Skip condition operators = >
        Skip condition (lower limit) = 70
        Skip condition upper limit =
        Skip next items = -1
        Default is skip =
Despike
        From Time =
        To Time =
        Signal = U
        Standard Deviations = 6
        Spike width = 8
        Spike % consistency = 50
        Replace spikes = x
        Storage Label spike count = spikeU
        Outlier Standard Deviations = 8
Despike
        From Time =
        To Time =
        Signal = V
```

```
        Standard Deviations = 6
        Spike width = 8
        Spike % consistency = 50
        Replace spikes = x
        Storage Label spike count = spikeV
        Outlier Standard Deviations = 8
Despike
        From Time =
        To Time =
        Signal = W
        Standard Deviations = 6
        Spike width = 8
        Spike % consistency = 50
        Replace spikes = x
        Storage Label spike count = spikeW
        Outlier Standard Deviations = 8
Despike
        From Time =
        To Time =
        Signal = Ts
        Standard Deviations = 6
        Spike width = 8
        Spike % consistency = 50
        Replace spikes = x
        Storage Label spike count = spikeT
        Outlier Standard Deviations = 8
Despike
        From Time =
        To Time =
        Signal = C
        Standard Deviations = 4
        Spike width = 12
        Spike % consistency = 30
        Replace spikes = x
        Storage Label spike count = spikeC
        Outlier Standard Deviations = 8
Despike
        From Time =
        To Time =
        Signal = Q
        Standard Deviations = 4
        Spike width = 12
        Spike % consistency = 30
        Replace spikes = x
        Storage Label spike count = spikeQ
        Outlier Standard Deviations = 8
Wind direction
        From Time =
        To Time =
        Signal (u) = U
```

```
        Signal (v) = V
        Orientation = 4
        Wind Direction Components = U+N_V+W
        Wind Direction Output = N_0_deg-E_90_deg
        Storage Label Wind Direction = WindDir
        Storage Label Wind Dir Std Dev = sdWindDir
Rotation - Planar
        From Time =
        To Time =
        Signal (u) = U
        Signal (v) = V
        Signal (w) = W
        w offset (b0) = 0.031962591
        Planar Alpha (b1) = 0.017057471
        Planar Beta (b2) = -0.08711226
Cross Correlate
        From Time =
        To Time =
        Signal = W
        Signal which lags = M
        Correlation type = Covariance
        Output Correlation curve =
        Storage Label Peak Time = MLag
        Storage Label Peak Value =
Remove Lag
        From Time =
        To Time =
        Signal = M
        Min Lag (sec) = 0.6
        Lag (sec) =
        Max Lag (sec) = 1.4
        Below Min default (sec) = 0.8
        Above Max default (sec) = 0.8
1 chn statistics
        From Time =
        To Time =
        Signal = U
        Storage Label Mean = meanU
        Storage Label Std Dev = sdU
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxU
        Storage Label Minimum = MinU
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = V
```

```
        Storage Label Mean = meanV
        Storage Label Std Dev = sdV
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxV
        Storage Label Minimum = MinV
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = W
        Storage Label Mean = meanW
        Storage Label Std Dev = sdW
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxW
        Storage Label Minimum = MinW
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = Ts
        Storage Label Mean = meanTs
        Storage Label Std Dev = sdTs
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxTs
        Storage Label Minimum = MinTs
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = C
        Storage Label Mean = meanC
        Storage Label Std Dev = sdC
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxC
        Storage Label Minimum = MinC
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
```

```
        To Time =
        Signal = Q
        Storage Label Mean = meanQ
        Storage Label Std Dev = sdQ
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxQ
        Storage Label Minimum = MinQ
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = Qc
        Storage Label Mean = meanQc
        Storage Label Std Dev = sdQc
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxQc
        Storage Label Minimum = MinQc
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = E
        Storage Label Mean = e
        Storage Label Std Dev = sde
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = Maxe
        Storage Label Minimum = Mine
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = Ta
        Storage Label Mean = MeanTa
        Storage Label Std Dev = sdTa
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxTa
        Storage Label Minimum = MinTa
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
```

```
1 chn statistics
        From Time =
        To Time =
        Signal = P
        Storage Label Mean = MeanP
        Storage Label Std Dev = sdP
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxP
        Storage Label Minimum = MinP
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
1 chn statistics
        From Time =
        To Time =
        Signal = M
        Storage Label Mean = MeanM
        Storage Label Std Dev = sdM
        Storage Label Skewness =
        Storage Label Kurtosis =
        Storage Label Maximum = MaxM
        Storage Label Minimum = MinM
        Storage Label Variance =
        Storage Label Turbulent Intensity =
        Alt Turbulent Intensity Denominator =
2 chn statistics
        From Time =
        To Time =
        Signal = W
        Signal = Ts
        Storage Label Covariance =
        Storage Label Correlation =
        Storage Label Flux = Ho
        Flux coefficient = 1160
Gas conversion time series
        From Time =
        To Time =
        Signal = M
        Convert from = Concentration umol/mol
        Convert to = Molar density umol/m3
        1st Offset = 0
        1st Gain = 1
        1st Curvature = 0
        Signal T, C =
        Value T, C = MeanTa
        Signal P, kPa =
        Value P, kPa = MeanP
        Signal H2O =
        Value H2O = meanQc
```

```
        Units H2O = Molar density mmol/m3
        Molecular Weight = 16
        2nd Offset = 0
        2nd Gain = 1
        2nd Curvature = 0
Virtual Temperature Raw
        From Time =
        To Time =
        Signal T(C) = Ts
        Signal H2O = Qc
        Pressure, kPa = MeanP
        Water vapour units = Molar density, mmol/m3
        Temperature conversion = Calculate true from virtual-sonic
Gas conversion
        From Time =
        To Time =
        Storage Label = e_fromIRGA
        Apply to =
        Apply by =
        Measured variable = meanQ
        Convert from = Absolute density g/m3
        Convert to = Partial Pressure kPa
        Temperature (C) = MeanTa
        Pressure (kPa) = MeanP
        Water vapour = e
        Water vapour units = Partial pressure kPa
        Molecular weight (g/mole) = 18
Sensible heat flux coefficient
        From Time =
        To Time =
        Storage Label = rhocp
        Apply to =
        Apply by =
        Vapour pressure (KPa) = e
        Min or QC =
        Max or QC =
        Temperature (C) = MeanTa
        Min or QC =
        Max or QC =
        Pressure (KPa) = MeanP
        Min or QC =
        Max or QC =
        Alternate rhoCp =
Latent heat of evaporation
        From Time =
        To Time =
        Storage Label = L
        Apply to =
        Apply by =
        Temperature (C) = MeanTa
```

```
          Min or QC =
          Max or QC =
          Pressure (KPa) = MeanP
          Min or QC =
          Max or QC =
          LE flux coef, L =
Friction Velocity
          From Time =
          To Time =
          Signal (u) = U
          Signal (v) = V
          Signal (w) = W
          Storage Label U* (uw) = ustar_uw
          Storage Label U* (uw vw) = ustar_uwvw
2 chn statistics
          From Time =
          To Time =
          Signal = W
          Signal = U
          Storage Label Covariance = uw
          Storage Label Correlation =
          Storage Label Flux =
          Flux coefficient =
2 chn statistics
          From Time =
          To Time =
          Signal = W
          Signal = Ts
          Storage Label Covariance =
          Storage Label Correlation =
          Storage Label Flux = H
          Flux coefficient = rhocp
2 chn statistics
          From Time =
          To Time =
          Signal = W
          Signal = C
          Storage Label Covariance =
          Storage Label Correlation =
          Storage Label Flux = Fc
          Flux coefficient = 1
2 chn statistics
          From Time =
          To Time =
          Signal = W
          Signal = Q
          Storage Label Covariance =
          Storage Label Correlation =
          Storage Label Flux = LE
          Flux coefficient = L
```

```
2 chn statistics
        From Time =
        To Time =
        Signal = W
        Signal = M
        Storage Label Covariance =
        Storage Label Correlation =
        Storage Label Flux = Fm
        Flux coefficient = 1
Stability - Monin Obhukov
        From Time =
        To Time =
        Storage Label = ZoL
        Apply to =
        Apply by =
        Measurement height (m) = Ht
        Zero plane displacement (m) = ZeroPlane
        Virtual Temperature (C) = meanTs
        Min or QC =
        Max or QC =
        H flux (W/m2) = H
        Min or QC =
        Max or QC =
        H flux coef, RhoCp = rhocp
        Min or QC =
        Max or QC =
        Scaling velocity (m/s) = ustar_uwvw
        Min or QC =
        Max or QC =
Tube attenuation
        From Time =
        To Time =
        Storage Label = TubeAtten
        Apply to =
        Apply by =
        Gas species = CH4
        Tube pressure (KPa) = 64
        Min or QC =
        Max or QC =
        Flow rate (LPM) = 12.5
        Tube length (m) =  6
        Tube ID (m) = 0.0043
        User defined Lambda coefficient =
Frequency response
        From Time =
        To Time =
        Storage Label = FreqResp_uw
        Apply to =
        Apply by =
        Correction type = UW
```

```
        Measurement height (m) = Ht
        Zero plane displacement (m) = ZeroPlane
        Boundary layer height (m) = 1000
        Stability Z/L = ZoL
        Wind speed (m/s) = meanU
        Sensor 1 Flow velocity (m/s) = meanU
        Sensor 1 Sampling frequency (Hz) = SampleFreq
        Sensor 1 Low pass filter type =
        Sensor 1 Low pass filter time constant =
        Sensor 1 High pass filter type =
        Sensor 1 High pass filter time constant =
        Sensor 1 Path length (m) = 0.1
        Sensor 1 Time constant (s) = 0
        Sensor 1 Tube attenuation coef =
        Sensor 2 Flow velocity (m/s) = meanU
        Sensor 2 Sampling frequency (Hz) = SampleFreq
        Sensor 2 Low pass filter type =
        Sensor 2 Low pass filter time constant =
        Sensor 2 High pass filter type =
        Sensor 2 High pass filter time constant =
        Sensor 2 Path length (m) = 0.1
        Sensor 2 Time constant (s) = 0
        Sensor 2 Tube attenuation coef =
        Path separation (m) = 0
        Get spectral data type = Model
        Get response function from = model
        Reference Tag =
        Reference response condition =
        Sensor 1 subsampled =
        Sensor 2 subsampled =
        Apply velocity distribution adjustment =
        Use calculated distribution =
        Velocity distribution std dev=
        Stability distribution std dev=
Frequency response
        From Time =
        To Time =
        Storage Label = FreqResp_H
        Apply to =
        Apply by =
        Correction type = WX
        Measurement height (m) = Ht
        Zero plane displacement (m) = ZeroPlane
        Boundary layer height (m) = 1000
        Stability Z/L = ZoL
        Wind speed (m/s) = meanU
        Sensor 1 Flow velocity (m/s) = meanU
        Sensor 1 Sampling frequency (Hz) = SampleFreq
        Sensor 1 Low pass filter type =
        Sensor 1 Low pass filter time constant =
```

```
    Sensor 1 High pass filter type =
    Sensor 1 High pass filter time constant =
    Sensor 1 Path length (m) = 0.1
    Sensor 1 Time constant (s) = 0
    Sensor 1 Tube attenuation coef =
    Sensor 2 Flow velocity (m/s) = meanU
    Sensor 2 Sampling frequency (Hz) = SampleFreq
    Sensor 2 Low pass filter type =
    Sensor 2 Low pass filter time constant =
    Sensor 2 High pass filter type =
    Sensor 2 High pass filter time constant =
    Sensor 2 Path length (m) = 0.1
    Sensor 2 Time constant (s) = 0
    Sensor 2 Tube attenuation coef =
    Path separation (m) = 0
    Get spectral data type = Model
    Get response function from = model
    Reference Tag =
    Reference response condition =
    Sensor 1 subsampled =
    Sensor 2 subsampled =
    Apply velocity distribution adjustment =
    Use calculated distribution =
    Velocity distribution std dev=
    Stability distribution std dev=
Frequency response
    From Time =
    To Time =
    Storage Label = FreqResp_FcLE
    Apply to =
    Apply by =
    Correction type = WX
    Measurement height (m) = Ht
    Zero plane displacement (m) = ZeroPlane
    Boundary layer height (m) = 1000
    Stability Z/L = ZoL
    Wind speed (m/s) = meanU
    Sensor 1 Flow velocity (m/s) = meanU
    Sensor 1 Sampling frequency (Hz) = SampleFreq
    Sensor 1 Low pass filter type =
    Sensor 1 Low pass filter time constant =
    Sensor 1 High pass filter type =
    Sensor 1 High pass filter time constant =
    Sensor 1 Path length (m) = 0.1
    Sensor 1 Time constant (s) = 0
    Sensor 1 Tube attenuation coef =
    Sensor 2 Flow velocity (m/s) = meanU
    Sensor 2 Sampling frequency (Hz) = SampleFreq
    Sensor 2 Low pass filter type =
    Sensor 2 Low pass filter time constant =
```

```
          Sensor 2 High pass filter type =
          Sensor 2 High pass filter time constant =
          Sensor 2 Path length (m) = 0.125
          Sensor 2 Time constant (s) = 0.1
          Sensor 2 Tube attenuation coef =
          Path separation (m) = 0.22
          Get spectral data type = Model
          Get response function from = model
          Reference Tag =
          Reference response condition =
          Sensor 1 subsampled =
          Sensor 2 subsampled =
          Apply velocity distribution adjustment =
          Use calculated distribution =
          Velocity distribution std dev=
          Stability distribution std dev=
Frequency response
          From Time =
          To Time =
          Storage Label = FreqResp_Fm
          Apply to =
          Apply by =
          Correction type = WX
          Measurement height (m) = Ht
          Zero plane displacement (m) = ZeroPlane
          Boundary layer height (m) = 1000
          Stability Z/L = ZoL
          Wind speed (m/s) = meanU
          Sensor 1 Flow velocity (m/s) = meanU
          Sensor 1 Sampling frequency (Hz) = SampleFreq
          Sensor 1 Low pass filter type =
          Sensor 1 Low pass filter time constant =
          Sensor 1 High pass filter type =
          Sensor 1 High pass filter time constant =
          Sensor 1 Path length (m) = 0.1
          Sensor 1 Time constant (s) = 0
          Sensor 1 Tube attenuation coef =
          Sensor 2 Flow velocity (m/s) = meanU
          Sensor 2 Sampling frequency (Hz) = SampleFreq
          Sensor 2 Low pass filter type =
          Sensor 2 Low pass filter time constant =
          Sensor 2 High pass filter type =
          Sensor 2 High pass filter time constant =
          Sensor 2 Path length (m) =  0.125
          Sensor 2 Time constant (s) = 0.1
          Sensor 2 Tube attenuation coef = TubeAtten
          Path separation (m) = 0.25
          Get spectral data type = Model
          Get response function from = model
          Reference Tag =
```

```
          Reference response condition =
          Sensor 1 subsampled =
          Sensor 2 subsampled =
          Apply velocity distribution adjustment =
          Use calculated distribution =
          Velocity distribution std dev=
          Stability distribution std dev=
Mathematical operation
          From Time =
          To Time =
          Storage Label = UWc
          Apply to =
          Apply by =
          Measured variable A = uw
          Operation  = *
          Measured variable B = FreqResp_uw
Mathematical operation
          From Time =
          To Time =
          Storage Label = Hc
          Apply to =
          Apply by =
          Measured variable A = H
          Operation  = *
          Measured variable B = FreqResp_H
Mathematical operation
          From Time =
          To Time =
          Storage Label = LEc
          Apply to =
          Apply by =
          Measured variable A = LE
          Operation  = *
          Measured variable B = FreqResp_FcLE
Mathematical operation
          From Time =
          To Time =
          Storage Label = Fcc
          Apply to =
          Apply by =
          Measured variable A = Fc
          Operation  = *
          Measured variable B = FreqResp_FcLE
Mathematical operation
          From Time =
          To Time =
          Storage Label = Fmc
          Apply to =
          Apply by =
          Measured variable A = Fm
```

```
        Operation  = *
        Measured variable B = FreqResp_Fm
Webb correction
        From Time =
        To Time =
        Storage Label = WPLc
        Apply to =
        Apply by =
        Scalar value type = Density (mg/m3)
        Scalar value = meanC
        Min or QC =
        Max or QC =
        Water vapour value type = Density (g/m3)
        Water vapour value = meanQ
        Min or QC =
        Max or QC =
        Temperature (C) = MeanTa
        Min or QC =
        Max or QC =
        Pressure (KPa) = MeanP
        Min or QC =
        Max or QC =
        H flux (W/m2) = Hc
        Min or QC =
        Max or QC =
        LE flux (W/m2) = LEc
        Min or QC =
        Max or QC =
        H flux coef, RhoCp = rhocp
        Min or QC =
        Max or QC =
        LE flux coef, L = L
        Min or QC =
        Max or QC =
        Scalar molecular wt. = 44
        Scalar flux type = Fx (mg/m2/s)
        Scalar flux coefficient = 1
        Min or QC =
        Max or QC =
        Alternate water vapour pressure (kPa) =
        Alternate temperature (C) =
        Alternate pressure (kPa) =
Webb correction
        From Time =
        To Time =
        Storage Label = WPLq
        Apply to =
        Apply by =
        Scalar value type = Density (g/m3)
        Scalar value =  meanQ
```

```
        Min or QC =
        Max or QC =
        Water vapour value type = Density (g/m3)
        Water vapour value = meanQ
        Min or QC =
        Max or QC =
        Temperature (C) = MeanTa
        Min or QC =
        Max or QC =
        Pressure (KPa) = MeanP
        Min or QC =
        Max or QC =
        H flux (W/m2) = Hc
        Min or QC =
        Max or QC =
        LE flux (W/m2) = LEc
        Min or QC =
        Max or QC =
        H flux coef, RhoCp = rhocp
        Min or QC =
        Max or QC =
        LE flux coef, L = L
        Min or QC =
        Max or QC =
        Scalar molecular wt. = 18
        Scalar flux type = LE (W/m2)
        Scalar flux coefficient = L
        Min or QC =
        Max or QC =
        Alternate water vapour pressure (kPa) =
        Alternate temperature (C) =
        Alternate pressure (kPa) =
Mathematical operation
        From Time =
        To Time =
        Storage Label = Fccw
        Apply to =
        Apply by =
        Measured variable A = Fcc
        Operation  = +
        Measured variable B = WPLc
Mathematical operation
        From Time =
        To Time =
        Storage Label = LEcw
        Apply to =
        Apply by =
        Measured variable A = LEc
        Operation  = +
        Measured variable B = WPLq
```

Appendix 2 – Soil CO_2 flux models with fitted parameters

Summer period

The exponential model (van't Hoff, 1884):

$$SF = R_b e^{\beta T} \tag{5.6}$$

If T is air temperature, $R_b = 0.58$ and $\beta = 0.0644$
If T is soil temperature at 8 cm depth, $R_b = 0.062$ and $\beta = 0.273$

The Arrhenius (1898) equation:

$$SF = R_{10} e^{E_0 T^{-1}} \tag{5.7}$$

If T is air temperature, $R_{10} = 2.95$ and $E_0 = -9.23$
If T is soil temperature at 8 cm depth, $R_{10} = 47.50$ and $E_0 = -39.64$

The Lloyd & Taylor (1994) modified Arrhenius model:

$$SF = R_{10} e^{E_0 (T_0 + T)^{-1}} \tag{5.8}$$

If T is air temperature, $R_{10} = 1342.61$, $E_0 = -710.39$ and $T_0 = 89.21$
If T is soil temperature at 8 cm depth, $R_{10} = 1361.37$, $E_0 = -154.86$ and $T_0 = 11.24$

Multiple regression model:

$$SF = (Ta) + (SMb) + c \qquad \textbf{(5.10)}$$

where a, b and c are regression coefficients.
If T is air temperature, a = 0.085, b = -1.709 and c = 1.618
If T is soil temperature, a = 0.303, b = -1.247 and c = -1.064

Winter period

The exponential model (van't Hoff, 1884):

$$SF = R_b e^{\beta T} \qquad \textbf{(5.6)}$$

When T is soil temperature at 2.5 cm depth, $R_b = 0.17$ and $\beta = 0.14$

The Arrhenius (1898) equation:

$$SF = R_{10} e^{E_0 T^{-1}} \qquad \textbf{(5.7)}$$

When T is soil temperature at 2.5 cm depth, $R_{10} = 0.90$ and $E_0 = -5.72$

The Lloyd & Taylor (1994) modified Arrhenius model:

$$SF = R_{10} e^{E_0 (T_0 + T)^{-1}} \qquad \textbf{(5.8)}$$

When T is soil temperature at 2.5 cm depth, $R_{10} = 1160.43$, $E_0 = -487.13$ and $T_0 = 55.21$