Scaling up of methane flux: a case study in the UK uplands

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Abstract

In the context of current and any future climate change, methane (CH_4) is an important greenhouse gas (GHG). However, current global trends of changes in atmospheric CH_4 are unpredictable and the relative contributions of individual global sources and sinks are inadequately quantified. If net CH_4 emissions are to be reduced, an improved understanding of key components, including natural wetlands, is required.

A study was conducted in order to construct an annual landscape estimate of CH_4 flux for a typical UK blanket bog site near to Lake Vyrnwy, North Wales. Flux measurements were made following an established chamber method and sampling was maintained throughout a calendar year and was spatially stratified by vegetation to facilitate landscape extrapolation. In order to identify which environmental variables controlled CH_4 fluxes from the blanket bog, regression analyses were performed using environmental variables measured at the time of flux measurement. In order to identify the longer term influence of environmental conditions, regression analyses were also conducted with running averages of measurements from periods prior to the day of flux measurement. A series of *in situ* experiments were undertaken to test hypotheses which examined the different controls on the observed variation in CH_4 fluxes, related to temporal and spatial patterns of CH_4 flux and to putative biases of sampling methods due to the limited footprint of chambers.

CH_4 fluxes displayed a distinct seasonal pattern with low mean fluxes from January until June, when a dramatic increase in net methane emission occurred; higher CH_4 fluxes continued until November and December. The site was a net source of CH_4 and the best landscape estimate of CH_4 flux (± standard error of the mean) was 9.8 (±3.8) g CH_4 m^{-2} $year^{-1}$. Errors associated with the extrapolation of measurements to a landscape-scale estimate resulted in estimates that ranged from 8.6 (±3.7) to 11.1 (±3.8) g CH_4 m^{-2} $year^{-1}$. Soil temperature and water table were the environmental variables which were most

consistently associated with CH_4 fluxes. However, the relationship between fluxes and water table did not always control CH_4 fluxes in an expected manner. At some sites CH_4 emissions were lower when the water table was closer to the surface, a result which contradicted the acrotelm-catotelm model of CH_4 flux, but may be explained by the hysteresis of fluxes in response to changing water table. Strong hysteresis of CH_4 fluxes was also apparent in response to temperature and radiation.

Hourly measurements of CH_4 flux showed high variability but no significant difference between measurements during day and night. Similarly, a replicated landscape-scale experiment of water table manipulation was expected to cause changes in CH_4 flux but, despite controlling for other aspects of spatial variation, the manipulation had no significant effect on CH_4 fluxes. Flux estimates were made using chambers with footprints that varied by three orders of magnitude and there was no significant effect on mean CH_4 fluxes. However, the variance of CH_4 flux estimates strongly correlated with sample area with markedly smaller variance as chamber size increased.

Overall estimates of landscape CH_4 flux were in the range of previous estimates made for UK peatland sites, but virtually all estimates displayed high variability. Such variability constrained the comparison of different estimates but it is possible to use methods, such as chambers with very large footprints, to improve the results of *in situ* studies.

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Author's declaration

I, James Edward Stockdale, hereby certify that I am the sole author of this thesis and that it has not been submitted in any previous application for a higher degree. This thesis is a record of the work carried out by me with the following exceptions.

I was responsible for the experimental design, installation and sampling for the repeated seasonal measurements used in Chapters 2 and 3 but was given technical field assistance by Phil Ineson, Syliva Toet, Anna Bing, Rob Holden, Cat Moody and Lorna Paterson. The maximum likelihood supervised classification used to calculate the proportional coverage of vegetation at the Lake Vyrnwy site was kindly performed by Natasha MacBean. I was involved in jointly involved in collecting the reference data and undertook the subsequent landscape-scale extrapolation of CH_4 fluxes seen in Chapter 2.

I was also responsible for the design, installation and completion of all three experiments in Chapter 4 however the comparison of different sized chambers was conducted jointly with Andreas Heinemeyer. Technical field assistance for these experiments was given by Phil Ineson, Sylvia Toet, Rob Holden, Cat Moody, Graham Hambley, James Stafford and Kate Storer.

Chapter 1 General Introduction

1.1 Historical context

The earliest scientific description of methane (CH_4) was made by Alessandro Volta in 1776 after collecting 'combustible air' by disturbing sediments at Lake Magiorre (Gest, 1987). A steady accumulation of knowledge regarding CH_4 has occurred over the intervening period and included several key observations. By 1787, Antoine Lavoiser had provided evidence that this gas was "carbonated hydrogen" (Wolfe, 1993) and in 1868 Antoine Béchamp provided the first evidence that CH_4 production was a microbiological process (Bechamp, 1868). Tyndall (1862) was the first to observe strong evidence of "calorific absorption" (*sensu* Tyndall, 1859) of radiant heat by CH_4 (known as marsh-gas); gases which display this property are now known as greenhouse gases (GHGs). This property was investigated by Arrhenius (1896) who presented the first calculations of how increases in a GHG (CO_2, known as carbonic acid) could lead to changes in global temperatures. Nielsen and Nielsen (1935) published details of the specific absorption bands of the infrared spectrum for CH_4 which subsequently enabled Migeotte (1948) to repeatedly observe that CH_4 was present in the atmosphere. Despite an understanding that atmospheric CH_4 was a result of biological sources, it was subsequently believed to be at a "constant percentage" of around 2 ppmv (Glueckauf, 1951).

Not until more than 30 years later were observations of the increasing atmospheric CH_4 concentration published. These include Rasmussen and Khalil (1981) who repeated CH_4 measurements during a 22 month period in a single location and found a substantial increase of around 2% per annum. Subsequent studies of past concentrations of atmospheric CH_4 have been able to place this rate of increase in a historical context. Modelled estimates of atmospheric CH_4 concentration extend back to the late Devonian (around 400 MA, see Beerling *et al.* 2009), but an extensive and directly observed record is available from the concentration of CH_4 in air bubbles which have been trapped inside polar ice. Measurements have been successfully retrieved from the last 802,000 years; a period which includes eight glacial and inter-glacial cycles (Loulergue *et al.* 2008). Whilst historical measurements from ice cores have been available since the 1970's (e.g. Robbins *et al.* 1973), the historically low concentrations of CH_4 were not initially interpreted as an indication of increases of atmospheric CH_4 in the intervening period, rather as a chemical transformation from CH_4 to CO in the ice itself (Robbins *et al.* 1973). As records of past CH_4 concentrations have been extended (e.g. Loulergue *et al.* 2008), and due to the observation that CO is present in freshly fallen snow (Khalil, 2000), the suggestion of an increasing concentration of atmospheric CH_4 is now widely accepted.

1.2 Global trends of atmospheric CH_4 concentration

Whilst it has taken just over 200 years to progress from an initial description of CH_4 to the observation that CH_4 is currently accumulating in the atmosphere at an unprecedented rate, it is only within the last three decades that the net accumulation of CH_4 in the atmosphere has been highlighted as an important global change issue. This is partially due to Tyndall's early observation (1862) that CH_4 is a potent GHG; the Global Warming Potential (GWP), which is a ratio of the warming that occurs as a result of radiative absorption by a gas (Radiative Forcing, RF, *sensu* Forster *et al.* 2007), of CH_4 is 21 times greater than CO_2 when considered over a 100 year period (Table 2.14 in Forster *et al.* 2007). After water vapour and CO_2, atmospheric CH_4 is considered the third largest contributor to the greenhouse effect (Trenberth *et al.* 2007). However, it will become increasingly important due to the relatively large amount of atmospheric CO_2 (379 ppm of CO_2 compared to 1.8 ppm of CH_4 in 2005; Forster *et al.* 2007) and asymptotic relationship between CO_2 concentration and RF which means the absorption of radiation becomes relatively smaller at higher atmospheric concentrations of CO_2 (see Fig. 4.5 in Archer, 2007).

The record of atmospheric CH_4 concentrations derived from ice cores together with direct observation since the 1970s (Rasmussen and Khalil, 1981), have shown that the global average CH_4 concentration of 1794 ppb in 2009 (Dlugokencky *et al.* 2011) was the highest since, at least, the mid-Pleistocene (Loulergue *et al.* 2008). This record also showed temporal variability of atmospheric CH_4 at many scales. For the majority of the last 800,000 years, atmospheric CH_4 displayed a close association with global temperature, and atmospheric CO_2, with a slowly decreasing concentration from 700 ppb during inter-glacial periods to 350 ppb during glacial periods (Loulergue *et al.* 2008). Yet, during the current inter-glacial period from *ca.* 5,000 years ago until the start of the industrial revolution *ca.* 1750 (a period known as the Late Pre-Industrial Holocene, *sensu* Mitchell *et al.* 2011), atmospheric CH_4 increased from around 580 ppb to 700 ppb (Sowers, 2010). The post-industrial revolution rate of increase has generally been much higher, with rates of increase reaching 1% per year in the 1970s and 1980s (Blake and Rowland, 1988). Since the 1990s the rate of increase has reduced to nearly zero, but with considerable inter-annual variation (Dlugokencky *et al.* 2003); however, atmospheric CH_4 was seen to start increasing again in 2007 and 2008 at a rate of around 0.5% per annum (Dlugokencky *et al.* 2003; Rigby *et al.* 2008). This complex pattern of recent increases has resulted in a current atmospheric CH_4 concentration of around 1800 ppb (Montzka *et al.* 2011) which is roughly 2.6 times higher than 1750 levels. As identified by Dlugokencky *et al.* (2011) this is proportionally much higher than other important GHGs such as CO_2 and N_2O which are about 1.3 and 1.2 times higher than pre-industrial levels, respectively (Jansen *et al.* 2007).

In addition to examining this complex pattern over different timescales, attempts to identity the drivers of change in atmospheric CH_4 are complicated by the diverse number of important sources and sinks of CH_4 (Wuebbles and Hayhoe, 2002). The concentration changes during the glacial and inter-glacial cycles and observed for the second half of the Quaternary Period (Loulergue *et al.* 2008) are thought to result from astronomically induced changes in insolation, known as the Milankovitch cycles (Khodri *et al.* 2001), amplified by other factors (Wolff *et al.* 2010). Consequently, attempts have been made to identify the relative contribution to changes in global temperatures either directly from changes in insolation, or from changes in atmospheric GHGs. For example, Yin and Berger (2012) showed the relative contribution to temperature changes varied between regions; changes in northern regions were driven by insolation, whereas changes in high southern latitudes were driven by GHGs.

Studies of the slow increase in atmospheric CH_4 during the Late Pre-Industrial Holocene, which started 5,000 years ago, have tested a variety of hypotheses including (i) a reduction in the tropospheric sink by OH radicals (Sowers, 2010), (ii) increases in wetland emission from tropical regions (Singarayer *et al.* 2011) and boreal regions (Chappellaz *et al.* 1997), and (iii) the early anthropogenic perturbation of the global CH_4 cycle through inefficient rice production (Ruddiman, 2003). Evidence supporting all of these hypotheses not only comes from absolute changes in atmospheric CH_4 but also from comparing ice cores from the Arctic (such as Greenland) and the Antarctic to identify changes in the inter-polar gradient (Chappellaz *et al.* 1997) and from changes in measurements of stable isotopes of atmospheric CH_4. This latter technique can be used to identify whether sources of CH_4 are biogenic (including wetlands), fossil or biomass burning (Ferretti *et al.* 2005).

Studies of the rapid post-industrial revolution increases in atmospheric CH_4 have produced similarly varied results, although the isotopic signature of increasing fossil emissions (Fletcher *et al.* 2004), estimates of the spatial distribution of emissions (Frankenberg *et al.* 2008), and estimates that current anthropogenic emissions are between 135% (Fletcher *et al.* 2004) and 255% (Chen and Prinn, 2006) higher than current ‘natural’ emissions, have resulted in little doubt that human activities are responsible for this dramatic increase (Forster *et al.* 2007). One debate regarding post-industrial revolution changes in atmospheric CH_4 has been fuelled by the observed slow-down in the rate of net accumulation which reached a nadir between 1990 and 2000 (Dlugokencky *et al.* 1998), before starting to increase again after 2007 (Dlugokencky *et al.* 2009). The diverse sources and sinks of atmospheric CH_4, which are known to contribute to the global CH_4 budget (Wuebbles and Hayhoe, 2002), are associated with an equally diverse range of potential hypotheses to explain this trend.

The overall reduction in atmospheric CH_4 has been attributed to a levelling-off of CH_4 emissions so that the atmosphere has been approaching a new 'steady-state' (Dlugokencky *et al.* 2011), a result of economic changes in the Soviet Union which affected emissions from fossil fuel production (Wang *et al.* 2004), or due to reduction in emissions associated with agriculture such as ruminants and rice production (Khalil and Rasmussen, 1993). Inter-annual variability has also been attributed to natural perturbations of climate, such as those following the Mount Pinatubo eruption (Dlugokencky *et al.* 1996) and El Niño conditions in 1997/1998 (Fletcher *et al.* 2004). The recent resumption of increasing atmospheric CH_4 may be a result of increasing emissions from the Arctic due to warmer temperatures (Rigby *et al.* 2008), or due to higher emissions from tropical wetlands experiencing higher levels of precipitation (Dlugokencky *et al.* 2011), and/or due to increased biomass burning (Dlugokencky *et al.* 2009).

1.3 Global CH_4 budgets

The overall rate of change in global atmospheric CH_4 is accurately known, thanks to coordinated sampling across global networks such as those operated by NOAA (Dlugokencky *et al.* 2009) and CSIRO (Langenfelds *et al.* 2002). However, studies of changing atmospheric CH_4, even when made over recent time periods, are unable to define the relative contribution of the wide number of sources and sinks to the 'bottom line' (Dlugokencky *et al.* 2009). The Intergovernmental Panel on Climate Change (IPCC) define three globally important sinks of CH_4 and 15 sources, which are divided into anthropogenic and natural categories (Table 7.6 in Denman *et al.* 2007).

Of the estimates of global budgets used by Denman *et al.* (2007), which includes estimates made from global sampling networks, spatiotemporal distribution of isotopic CH_4 ratios (known as 'top-down'), and estimates constructed from known components ('bottom-up'), the largest single anthropogenic source of CH_4 is from ruminants (enteric fermentation mainly from cattle but also sheep, water buffalo and goats; Lerner *et al.* 1988) and ranges from 76 (Scheehle *et al.* 2002) to 189 Tg CH_4 year^{-1} (Chen and Prinn, 2006). Estimates of emissions from the energy industry, which includes leakage from the extraction and production of coal, gas and oil, are typically the next largest anthropogenic source but, with a minimum of 74 Tg CH_4 year^{-1} (Scheehle *et al.* 2002) and maximum of 106 Tg CH_4 year^{-1} (Wuebbles and Hayhoe, 2002), are much less varied than estimates of other sources. One of the most variable estimates of CH_4 emissions are from rice agriculture; Scheehle *et al.* (2002) estimate a total of 31 Tg CH_4 year^{-1}, whereas other estimates can be as high as 112 Tg CH_4 year^{-1} (Chen and Prinn, 2006). The variability of rice agriculture estimates may be due to: (i) differences in methodology in calculating estimates, such as the different factors used to calculate net CH_4 flux from the amount of carbon returned to the soil (Wang *et al.* 2004); or (ii) temporal variation of emissions during different time periods when estimates are made. For example, the studies used by the IPCC relate to estimates of CH_4 emissions from various years between 1983 and 2001. This was a period of changing rate of increase of atmospheric CH_4 and, therefore, likely to be a period of changing emission from one or more of the global sources. Changes in irrigation (Li *et al.* 2002), fertilization (van der Gon, 1999), and crop varieties used (van der Gon, 2000) may have all influenced CH_4 emissions from rice agriculture at a global scale, thus increasing the variability between estimates over different time periods.

The remaining major anthropogenic sources of CH_4 are those from waste management (including landfill and wastewater handling), where estimates range from 35 (Fletcher *et al.* 2004) to 69 Tg CH_4 year^{-1} (Scheehle *et al.* 2002); and biomass burning, which produces CH_4 due to incomplete combustion (Hein *et al.* 1997), where estimates ranged from 14 (Scheehle *et al.* 2002) to 88 Tg CH_4 year^{-1} (Fletcher *et al.* 2004).

The natural sources of CH_4 are dominated by wetland emissions with estimates which range from 100 (Wuebbles and Hayhoe, 2002) to 231 Tg CH_4 year^{-1} (Fletcher *et al.* 2004). In comparison, the highest estimates used by the IPCC are no higher than 29 Tg CH_4 year^{-1} from termites (Fletcher *et al.* 2004), 15 Tg CH_4 year^{-1} from oceanic sources (Houweling *et al.* 2000), 15 Tg CH_4 year^{-1} from wild ruminants (Houweling *et al.* 2000), 14 Tg CH_4 year^{-1} from geological sources (Wuebbles and Hayhoe, 2002), 5 Tg CH_4 year^{-1} from hydrates and 5 Tg CH_4 year^{-1} from wildfires (both from Houweling *et al.* 2000).

The estimate of CH_4 emissions from wetlands is the largest single global source (Table 7.6 in Denman *et al.* 2007) and is the summation of emissions from diverse types of ecosystems which are widely distributed over the globe (see Plate 1 in Matthews and Fung, 1987). The different environmental conditions in these wetland types result in large differences in net ecosystem productivity (Whiting and Chanton, 1993) and globally, CH_4 emissions from wetlands are highly sensitive to changing environmental conditions (Cao *et al.* 1998). In addition, temporal variation in CH_4 emissions from wetlands may also produce variable global estimates. For example, the estimate by Fletcher *et al.* (2004) was of emissions during 1998 and 1999, a period including an unusually high increase in atmospheric CH_4 linked to changing climatic conditions associated with El Niño conditions in 1997/1998, possibly increasing wetland emissions (Bousquet *et al.* 2006). This suggests that the high CH_4 flux from wetlands estimated by Fletcher *et al.* (2004) may not be representative of 'normal' global conditions; however, other estimates of fluxes from different time periods often still result in similarly large wetland emissions (Hein *et al.* 1997; Bergamaschi *et al.* 2001).

As if to highlight the uncertainty of the components of the global CH_4 budget, considerable recent debate has been made with regard to the existence, or not, of a previously undescribed CH_4 source(s) which may represent up to 21% of all global emissions (Houweling *et al.* 2000). Using column-averaged concentrations of atmospheric CH_4 derived from SCIAMACHY , an instrument on board the ENVISAT satellite, and comparing the results with *a priori* global CH_4 budgets, Frankenberg *et al.* (2005) suggested a previously unknown source of CH_4 situated in tropical forests. A candidate CH_4 source was identified from a physiological study but was highly contentious as, in contrast to all other biogenic sources which are thought to require anoxic conditions (Conrad, 1996), it was suggested that CH_4 may be released by living plant tissue under oxic conditions (Keppler *et al.* 2006). Subsequently, studies made at varying scales have concluded that the existence of such a process was unlikely (Dueck *et al.* 2007; Bloom *et al.* 2010a), yet other observations of aerobic CH_4 production (e.g. Mcleod *et al.* 2008) supported this novel claim. An updated calculation of terrestrial CH_4 exchange from the satellite-borne measurements of atmospheric CH_4 was published by Frankenberg *et al.* (2008) and indicated that the previously identified increase in CH_4 emission from the tropics was erroneously increased due to interference of water vapour (their Fig. 3). Further contradictory results have recently been published (Gauci *et al.* 2010; Wang *et al.* 2011) and a mechanism of CH_4 production has yet to be clearly identified (Bruhn *et al.* 2012) suggesting further research is required to identify the scale of any contribution to the global CH_4 budget. However, the most pertinent study may be that by Frankenberg *et al.* (2008) which reduced the size of the unknown source of CH_4 from the tropics in the original study by Frankenberg *et al.* (2005), precipitating the current debate.

1.4 Peatlands as a source of CH_4 and store of carbon

The global CH_4 budget includes a diverse range of CH_4 sources (Wuebbles and Hayhoe, 2002). However, several important sources, including emissions from wetlands, termites, ruminants, waste management and rice agriculture, are all a result of similar processes of microbial (biogenic) CH_4 production (Conrad, 1996). As microbial CH_4 production is thought to be a strictly anoxic process (Lai, 2009), the observed association between wetlands and CH_4 emission (Morrissey *et al.* 1994) is subsequently expected. The importance of wetlands as a major global source of CH_4 (Denman *et al.* 2007) and the sensitivity of CH_4 emissions from wetlands to changing environmental conditions (Cao *et al.* 1998) make estimates of emissions from all wetland types important. In order to better characterise globally distributed wetlands sub-classifications have been used, such as the 28 wetland-vegetation classes used by Matthews and Fung (1987), and the more-broadly defined three-class system of swamps, bogs and tundra used by Wang *et al.* (2004). This latter classification is primarily defined by latitude, with swamps occurring in tropical and sub-tropical regions, bogs typically occurring in temperate regions, and tundra occurring in the high northern latitudes (Wang *et al.* 2004).

As wetlands in temperate and high latitudes are currently experiencing (Trenberth *et al.* 2007), and predicted to experience (Holland and Bitz, 2003), strong climate change in response to increasing levels of GHG, it is imperative that CH_4 fluxes from these regions are well characterised. Another feature of the classification used by Wang *et al.* (2004) is that they are peatlands, a sub-group of wetlands which all contain significant deposits of carbon (C) (Gorham, 1991). Estimates of the total amount of C globally stored in all soils vary between 1220 Pg C (Sombroek *et al.* 1993) and 1576 Pg C (Eswaran *et al.* 1993), but typically only include estimates of soils to 1 m below the surface (Post *et al.* 1982). This method ignores the significant amounts of C stored in peatlands at depths below 1 m (up to a maximum of 25 m; Zimov *et al.* 2006) and may underestimate actual global storage. For example, an estimate of all soil C within the large northern circumpolar permafrost suggests that this region may contain 1672 Pg C (Tarnocai *et al.* 2009). Regardless of approach, estimates of peatland C storage are typically equal to, or greater than, the combined amount of C currently residing in the atmospheric and vegetation pools (1360 Pg C; Schimel, 1995). As Raupach and Canadell (2010) succinctly described the process, "life on Earth has created vast stores of detrital carbon". The fate of this major global C store is critical within the context of a rapidly changing climate (Meehl *et al.* 2007) and potential emissions to the atmosphere as CH_4 (Zimov *et al.* 2006), a potent GHG.

The process of CH_4 production within peat soils, and subsequent transport to the atmosphere is well described (Le Mer and Roger, 2001), with the anoxic decomposition of organic material in the layers of soil beneath the water table (known as the catotelm) resulting in methanogenesis (Clymo, 1984). The three known catabolic pathways of methanogenesis, defined by the principal substrate, are acetotrophy, CO_2-reduction and methylotrophy (Boone *et al.* 1993), but in most peat soils the majority of CH_4 production is thought to be a result of acetotrophy (Bridgham and Richardson, 1992). In contrast, the oxidation of CH_4 (methanotrophy) is thought to occur in aerobic conditions in the layers of soil above the water table, known as the acrotelm in peatland systems.

In addition to the production and oxidation of CH_4, one other important component of the exchange of CH_4 exchange within the soil-plant-atmosphere continuum is the transport of CH_4 from sites of production in deeper areas to the atmosphere as summarised in Fig. 1.1. The method of transport to the atmosphere is key; one potential pathway is the diffusion of CH_4 from the catotelm through the acrotelm, but as CH_4 passes through aerobic soil conditions it is possible that a large proportion is consumed prior to being emitted to the atmosphere (Whalen and Reeburgh, 2000; Teh *et al.* 2005). In addition to diffusion, a major pathway for CH_4 is transportation through plant vascular structures, which contain

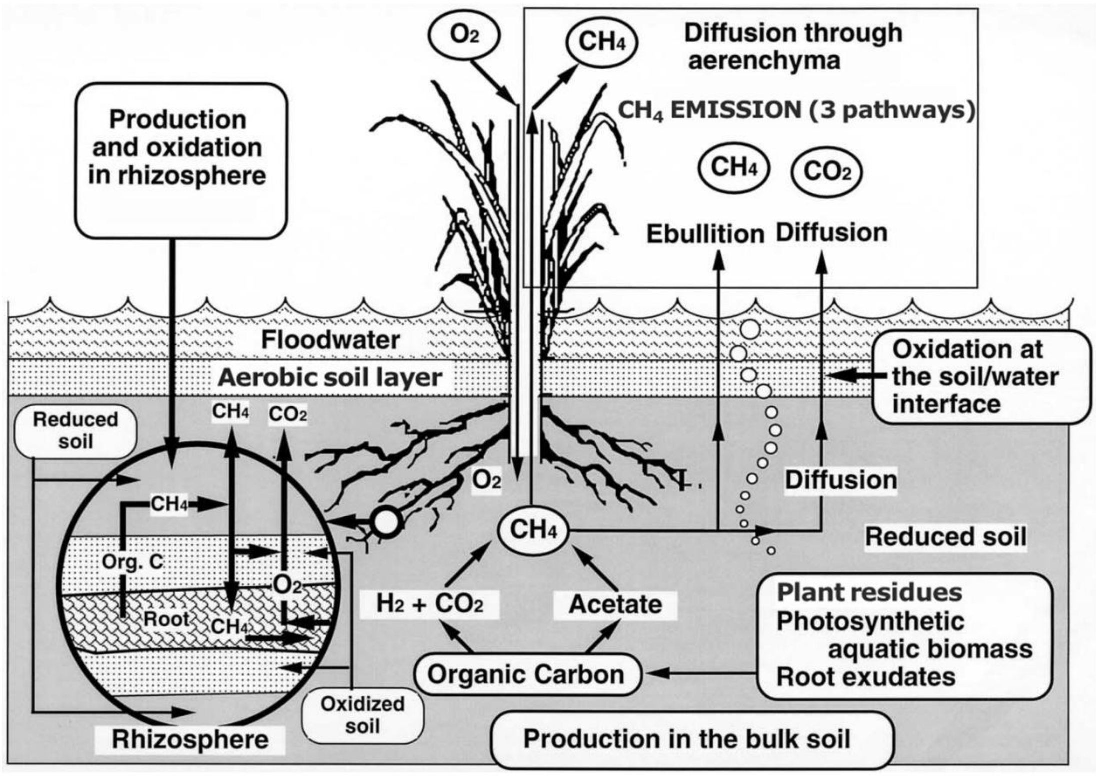

Fig. 1.1 A summary of methane production and transport pathways to the atmosphere via diffusion, aerenchymous tissue and ebullition. CH_4 is produced in the water-saturated anaerobic layer of soil (catotelm) and may also be consumed in any aerobic layer of soil above the water table (acrotelm). Adapted from Le Mer and Roger (2001).

porous aerenchymous tissue (Strom *et al.* 2003). Additionally, if the soil is water saturated, the formation and movement of bubbles of CH_4 can be important; a process known as ebullition (Kellner *et al.* 2006). Regardless of the controversial suggestion that CH_4 is actually produced from living plant tissue (see above), aerenchyma are structures which have evolved in some plant species to transport O_2 to roots which may experience anaerobic conditions (Armstrong *et al.* 1991) and are known pathways through which above-ground vegetation influences net CH_4 flux (Greenup *et al.* 2000). The acrotelm-catotelm model of CH_4 production and oxidation (Clymo, 1984), combined with the known pathways of transfer to the atmosphere (Topp and Pattey, 1997), provide a theoretical understanding of how net CH_4 flux from peatlands is derived.

1.5 Measurement methods

The empirical measurement of CH_4 fluxes from peatlands has been achieved using a variety of methods which vary in both scale and resource requirement. The smallest scale of measurement is usually achieved using extracted samples of soil, which are monitored under laboratory conditions. As samples are removed from natural conditions, without any vegetation which may provide aerenchymous transport (Lai, 2009), a common aim of these studies is to quantify potential rates of methane production and oxidation (e.g. Yrjala *et al.* 2011). Whilst the observations of high potentials for methane production are expected because of the microbial methanogen populations which reside in wet, anaerobic soils, results showing high oxidation potentials from methanotroph populations in similar environments are more surprising (see King *et al.* 1990). High net oxidation rates have often been observed in dry forest soils (e.g. Wang and Ineson, 2003), however, even under predominantly anaerobic conditions the strong supply of CH_4 substrate appears to enable considerable development of methanotroph populations which reduce the net emission of CH_4 observed in peatland sites (Sundh *et al.* 1994).

In addition to soil samples, mesocosms of peatland systems, which include vertical sections of soils with intact vegetation, have been extracted from peatlands and maintained and measured under laboratory conditions. Mesocosms may vary greatly in size and incubation conditions from the very basic, such as storing outside (Dinsmore *et al.* 2009b), to more complex, fully replicated, individually controllable environment facilities (such as the Ecotron facility; Lawton, 1996). Regardless of size and complexity, such studies are often used to identify the responses of CH_4 fluxes to experimental manipulation of conditions. Mesocosm studies have revealed clear responses of CH_4 flux in peatland systems to many environmental drivers including water table (Blodau and Moore, 2003a) and temperature (White *et al.* 2008). In addition to revealing underlying ecosystem processes, these studies help to indicate the potential response of systems to changes in climate (Updegraff *et al.* 2001) and land management (Freeman *et al.* 1993). However, as samples have to be extracted and transported from field sites, with incubation conditions tending to be uniformly controlled, they can be criticised for not realistically representing natural conditions (Blodau and Moore, 2003a).

In situ measurements and studies of CH_4 fluxes have been made in an attempt to provide representative flux estimates in a variety of peatlands including tundra (Mastepanov *et al.* 2008), boreal (Bubier *et al.* 1993), temperate (Teh *et al.* 2011) and tropcial (Jauhiainen *et al.* 2008) locations. Methods of measurement have been varied but approaches are dominated by either the enclosure of an area of soil (and any above ground vegetation) within a chamber (e.g. Leppala *et al.* 2011), or the use of micrometeorological methods (e.g. Baldocchi *et al.* 2012; Hendriks *et al.* 2007; Hendriks *et al.* 2010; Herbst *et al.* 2011). Chambers of varying sizes can be used to measure fluxes from various sizes of enclosed area or “footprint” (typically less than 1 m^2), but one difference between chamber studies often relates to the method of chamber operation; fluxes can either be determined by differences between gas concentration flowing into the chamber and the concentration flowing out (known as steady state), or fluxes calculated by the rate of change in gas concentration once a chamber has been sealed on the soil surface (known as non-steady state; Davidson *et al.* 2002). A further difference between non-steady state chambers is whether they are dynamic, which circulate air from the chamber to an external *in situ* gas analyser, or static, which do not circulate the air within the chamber, instead relying on the extraction, storage and transport of gas samples for subsequent laboratory analysis. Differences in the measured fluxes using either approach do not typically vary greatly (Moore and Roulet, 1991; Pumpanen *et al.* 2004) but care needs to taken in order to reduce the biases of each particular sampling method. For example, non-steady state chamber methods can underestimate emissions if increased headspace concentration of CH_4 leaks out leaks out during measurement (Tingey *et al.* 2000).

Flux measurements made with micrometeorolgical methods are the integrated value from a much larger footprint when compared to chambers and typically record greater temporal diversity. Micrometeroglical flux measurements are made with equipment mounted on stationary towers, which limits their spatial flexibility, but have also been mounted on airborne platforms to incorporate even larger footprints (Hill *et al.* 2011). All methods of *in situ* measurement have been used to follow spatial and temporal trends, but can also be used with experimental manipulations, such as alteration of temperature, rainfall and atmospheric CO_2 (Carter *et al.* 2011), or transplantation of mesocosms to contrasting conditions (Yavitt *et al.* 2005).

As the major purpose of *in situ* measurements is to produce unbiased, representative field estimates of fluxes, it is vital to minimise, or adjust for, biases in any method. Even if all measurement bias was removed, *in situ* measurements of CH_4 flux still present formidable challenges, as variability of estimates is often found to be very large (Prieme *et al.* 1996). This reflects the heterogeneity of CH_4 fluxes, which as they are the result of microbial-scale processes have been observed to display micro-scale variation (Wachinger *et al.* 2000). This variation hinders the identification of underlying controls over CH_4 fluxes in natural conditions (Ward *et al.* 2007), and contributes to the wide range in estimates seen at all scales (Blodau and Moore, 2003b; Polson *et al.* 2011).

1.6 Summary

The current increases in GHGs are a relatively recently identified global change issue. Whilst not being the largest contributor to the greenhouse effect, the high level of radiative forcing for CH_4 is one of the reasons that CH_4 is being recognised as an important target for reducing anthropogenic climate change (Shindell *et al.* 2012). Current global trends of changes in atmospheric CH_4 are unpredictable and poorly understood with relative contributions of individual sources and sink inadequately quantified and, if net CH_4 emissions are to be reduced, an improved understanding of key components is required.

Wetlands are an important global source of CH_4, but estimates of the global CH_4 emission from wetlands vary considerably. Despite the advanced nature of estimates of global CH_4 budgets (Olivier *et al.* 2005), observation is still a key research need for many components of the carbon cycle (Canadell *et al.* 2010). In a recent study of knowledge gaps regarding C and nitrogen (N) interactions in the soil at different scales, Gardenas *et al.* (2011) conclude that "reliable quantification of GHG emissions at the ecosystem scale is of paramount importance". Consequently, this study includes an attempt to make a landscape estimate of CH_4 fluxes at a typical peatland site in the UK and compare with previous estimates. Flux measurement techniques and methods of subsequent extrapolation need further improvement, particularly to overcome problems of estimating CH_4 fluxes in heterogeneous landscapes such as peatlands. This study also includes attempts to utilise novel measurement techniques to explain the observed variation in CH_4 fluxes and to increase the reliability of flux estimates.

The site selected for all *in situ* measurements in this study was a 22 km^2 area of upland blanket bog near to Lake Vyrnwy in North Wales. In addition to representing a typically heterogeneous peatland landscape within which to study CH_4 fluxes, the site was also a major scientific platform for a variety of other peatland studies. Whilst the site was extensively used by several projects which were part of the UK Population Biology Network (UKPopNet), it was also a platform for studying the impact of landscape-scale management changes on a variety of ecosystem services which are provided by the UK uplands.

Chapter 2 Landscape-scale estimate of greenhouse gas fluxes - a case study

2.1 Introduction

Since the establishment of individual sampling programmes demonstrating that atmospheric greenhouse gas (GHG) concentrations are increasing (such as Keeling, 1960 for CO_2 and Rasmussen and Khalil, 1981 for CH_4) and their subsequent geographical expansion into global sampling networks (such as that run by the National Oceanic and Atmospheric Administration (NOAA), for example Hein *et al.* 1997), it could be considered that the observation of the global atmospheric pools of CO_2 and CH_4 has been achieved. However, whilst current atmospheric concentrations can be placed within a historical context (Loulergue *et al.* 2008) and some seasonal, inter-annual and continental scale variations have been identified using such networks (such as Dlugokencky *et al.* 1998), these observations are limited in helping our understanding of the current processes that contribute to the overall exchange of GHG with the atmosphere. For example, the use of global observation networks identified a slow-down in the rate of atmospheric CH_4 increases during the 1990s (Dlugokencky *et al.* 1998) but the low resolution at which spatial variation had been observed resulted in a large number of conflicting hypotheses to explain this reduction. These include (i) the reduction in emissions from ruminants and from rice production (Khalil and Rasmussen, 1993; Dlugokencky *et al.* 1994); (ii) changes in fossil fuel production in former Soviet Union and Eastern Europe (Dlugokencky *et al.* 1994; Hein *et al.* 1997); (iii) reduced venting during oil production in Organization of the Petroleum Exporting Countries (OPEC) (Dlugokencky *et al.* 1994); and (iv) changes in temperature, precipitation and atmospheric chemistry due to the 1991 Mount Pinatubo eruption (Dlugokencky *et al.* 1994). The subsequent use of alternative estimates (in this case derived from demographic, social, economic and land use factors as well as ground-based measurements (Olivier 1994)) have been used to support the hypothesis that the

1990's reduction was due to falling emissions from the former Soviet Union (Dlugokencky *et al.* 2003) but without additional methods of budget construction, the question remains an open one.

The development of another 'top-down' method to measure GHG has increased understanding of fluxes in and out of the atmospheric pool, namely, satellite-borne measurements of trace gas concentrations. The first combined satellite-borne measurements of CH_4 and CO_2 were made using SCIAMACHY, launched onboard the ENVISAT satellite in 2002 to measure atmospheric concentration of CH_4 and CO_2 at a ground-scale of 60 km by 30 km (Frankenberg *et al.* 2005; Schneising *et al.* 2011). SCIAMACHY measures vertical columns of atmosphere over the entire globe in 6 days (Frankenberg *et al.* 2005) and provides observations which are starting to increase the understanding of anthropogenic influences, such as rice cultivation (Zhang *et al.* 2011) or burning of fossil fuels (Bovensmann *et al.* 2010), and natural influences, such as emissions from mud volcanoes (Georgoulias *et al.* 2011), on CH_4 fluxes at a regional scale. Early problems with the algorithm used to estimate fluxes have been rectified (Frankenberg *et al.* 2008). However, satellite-borne measurements, with a pixel size of 1800 km^2, are still not suited to identifying the impact of specific anthropogenic behaviours on CH_4 fluxes nor identifying highly spatially variable CH_4 fluxes which have been observed to occur in spatially small hotspots of activity (Bubier *et al.* 1993; McNamara *et al.* 2008; Leppala *et al.* 2011). For example, felling of trees in a temperate forest has been shown to significantly reduce CH_4 oxidation rates, whereas thinning trees led to an increase in CH_4 oxidation (Bradford *et al.* 2000). Consequently, the distinction between felling and thinning is important when constructing GHG budgets for temperate forest sites yet, given the typical scale of forest felling and thinning, it could not be made using satellite-borne measurements. An example of highly spatially variable CH_4 fluxes was provided by Dinsmore *et al.* (2009a) who estimated that within a distance of 0.6 km in a low-lying raised bog, CH_4 fluxes varied from 0.07 to 5.13 g CH_4 m^{-2} $year^{-1}$ in different microtopographic classes. The identification of which classes were responsible for significant proportions of fluxes (one class covered 0.5% of the spatial area but was responsible for 12% of CH_4 emissions) could only be achieved through measurements at a suitably fine scale.

The limitations of global sampling networks and satellite-borne measurements are potentially countered through the complimentary use of 'bottom-up' approaches. If measurements are used to make estimates of fluxes from all possible sources and sinks for a particular GHG, it is possible to create a full global budget for comparison with global changes (Wuebbles and Hayhoe, 2002), and to precisely identify how a single source or sink changes over time. Understanding the flux components of GHG budgets is essential for those stakeholders, including high-level policy makers with a desire to prevent further increases in atmospheric concentration (IPCC, 2007), or for individual land managers with a desire to assess the influence of management techniques on C exchanges in a variety of environments (Dobbie *et al.* 1996; Dannenmann *et al.* 2007; Ward *et al.* 2007). Even though tall tower and aircraft-mounted measurements have been used to make regional or continental scale estimates (for example, see Hill *et al.* 2011) all 'bottom-up' measurements are limited to single spatial points and always need to be extrapolated into estimates of a wider area. Careful consideration of the number and location of sampling points is needed to ensure samples are spatially representative, particularly in heterogeneous landscapes. Samples also need to represent any temporal variation, something which, even in relatively accessible landscapes within the UK, is rarely achieved. Of the 'bottom-up' approaches used by the IPCC in their Fourth Assessment Report (see Fig. 7.7 in Denman *et al.* 2007) estimates of CO_2 fluxes (such as Janssens *et al.* 2003) are based on direct measurements of fluxes by eddy covariance flux towers which include measurements throughout several annual cycles (see, for example, Valentini *et al.* 2000; Baldocchi *et al.* 2001). Valentini *et al.*'s (2000) study of CO_2 fluxes from European forests also included a range of spatial variation with 15 sites used ranging from 41 °N to 64 °N and 20 °W to 24 °E, whilst Baldocchi *et al.*, and the references therein, included full annual measurements from 34 sites in Europe, North and South America and Asia (2001). In contrast, the 'bottom-up' estimates of CH_4 fluxes used by the IPCC are more limited, with a single review used for estimates of global CH_4 fluxes from wetlands (Wuebbles and Hayhoe, 2002). This estimate was taken from Khalil (2000), who in turn took it from Matthews (2000), who derived it from three studies (Matthews and Fung, 1987; Aselmann and Crutzen, 1989; Bartlett *et al.* 1989) that had estimates which 'converged around 100 Tg CH_4 year^{-1}'. Mathews and Fung (1987) made an estimate of ca. 110 Tg CH_4 year^{-1} for the global CH_4 fluxes from wetlands which used five classes of wetlands (nonforested bog, forested bog, nonforested swamp, forested swamp, and alluvial). Whilst their study focused on developing methods of identifying the spatial distribution of wetlands, they choose typical fluxes for each class of wetland from just four studies. The class which data from the current study would be assigned to, nonforested bog, was represented by two studies. The first (Svensson, 1980) took measurements from an ombrotrophic mire in Sweden between 31st May and 7th September 1974, whilst the second (Sebacher *et al.* 1986) took a transect of measurements across Alaska during August 1984. Aselmann and Crutzen (1989) used data from 20 studies, divided into seven classes of wetlands (bogs, fens, swamps, marshes, floodplains, lakes and rice paddies) to make a global CH_4 flux from wetlands of between 40 and 160 Tg CH_4 year^{-1}. Of the 20 twenty studies used, three were included which took 'yearly' measurements. The class which the current study would have been assigned to is the 'bog' class and was represented by four studies. Of these four studies, only Clymo and Reddaway (1971) took measurements outside of the months May to September as they measured from October to April at intervals greater than a month. Bartlett *et al.* (1989) updated the estimate made by Mathews and Fung (1987) by including an additional 14 studies of wetland CH_4 fluxes, three of which are described as having 'annual data'. Of the studies in ‘non-forested bogs, no measurements were made outside of June to September. The final estimate by Bartlett *et al.* (1989) was 111 (±125) Tg CH_4 year^{-1} but uncertainty estimates were considered to be conservative as they did not include errors in the calculation of global coverage of wetland areas. As a result of the current limited availability of representative CH_4 flux data, the current study was designed to focus upon CH_4 fluxes from a typical upland blanket bog of the UK. Despite containing a very high proportion of the UK’s soil C stocks (Bellamy *et al.* 2005; Bradley *et al.* 2005) and having a high potential for high trace gas emissions (Macdonald *et al.* 1996; Lloyd *et al.* 1998), only one previous study has measured CH_4 fluxes throughout an entire annual cycle in an upland blanket bog (Ward *et al.* 2007).

The study presented here attempts to estimate the terrestrial fluxes of CH_4 and dark ecosystem respiration from a 22 km^2 area of upland blanket bog in Wales during a single calendar year. This landscape is heterogeneous at many scales with elevation varying from 300 to 550 m above sea level, whilst the site has been managed for a variety of economic purposes. For example, since the early 1990s, the vegetation has been mown to provide a mixture of habitats for bird species conservation (Bowker *et al.* 2007). From a microbial perspective, central to the production and consumption of CH_4, there is even greater heterogeneity as the varied microtopography results in a mixture of hydrological conditions and peat depths (Wilson *et al.* 2010). Additionally, the variation in vegetation provides a mixture of substrate inputs and transport mechanisms for atmospheric CH_4 emissions (Greenup *et al.* 2000; Hornibrook *et al.* 2009).

The current study used 0.038 m^2 chambers for sampling fluxes at a monthly frequency, with the objective of making a representative estimate of the entire landscape CH_4 flux. In meeting this challenge, the approach used was to stratify the sampling areas with dominant ecotypes and using a remotely sensed imaging of the entire landscape to enable proportional spatial extrapolation. Each ecotype was identifiable by dominant vegetation type and identified under the following National Vegetation Community types (Rodwell *et al.* 1991): heather, dominated by *Calluna vulgaris* and categorised as M19b; grass, dominated by species of *Molinia*, M24; Juncus, dominated by species of *Juncus*, M23b; or sedge, dominated by species of *Eriophorum*, M20a.

The main aim of this study was to produce annual estimates, with error terms, of CH_4 flux and dark ecosystem respiration (which will be subsequently referred to as respiration) for 22 km^2 of upland blanket bog in the UK. In addition, hypotheses that CH_4 flux and respiration were significantly different when (i) measured in areas dominated by different vegetation, or (ii) measured during different months of the year were also tested.

2.2 Materials and methods

2.2.1 Study site description

The study site was close to Lake Vyrnwy in the Berwyn Mountains of North Wales (SH 97661 22002) which falls within a Royal Society of the Protection of Birds (RSPB) Reserve, a National Nature Reserve (NNR), Site of Special Scientific Interest (SSSI), Special Protection Area (SPA) and Special Area of Conservation (SAC). Between 1961 and 1990, annual air temperature was 6.4 °C and annual rainfall 1501 mm (Freitag *et al.* 2010), with the initiation of blanket bog growth in the Berwyn Mountains due to changing climate rather than deforestation (Charman, 2002). Within the Reserve, the study area was limited to 22 km^2 of blanket bog and sampling was focused around three meteorological stations, with four identified vegetation types within a 20 m radius of the station (see Fig. 2.1): Eunant (SH 92336 22015), Hafod (SH 96619 21523) and Hirddu (SH 94839 21011).

2.2.2 Flux measurements

Static non-steady state chambers (for example see Holland *et al.* 1999; Bradford *et al.* 2001; Leppala *et al.* 2011; Toet *et al.* 2011) were employed for monthly measurements of methane flux and respiration between December 2008 and January 2010 from four vegetation types around each meteorological station. Five flux measurements were made at each combination of site and vegetation type to ensure measurements were representative and to enable failed measurements to be discarded. Circular collars, 20 cm diameter and 20 cm height, were inserted to a mean (±standard error of the mean, SEM) depth of 2.96 (±0.23) cm during August 2008, 3 months prior to the first measurements being taken with 25 cm high chambers of the same diameter. Sand (Building sand, B&Q, Eastleigh, Hampshire, UK) was packed around the exterior of each collar to enhance the seal between collar and soil surface. Collars and chambers were constructed from opaque polyvinyl chloride (PVC) piping, the chambers also included a PVC lid, sealed with solvent

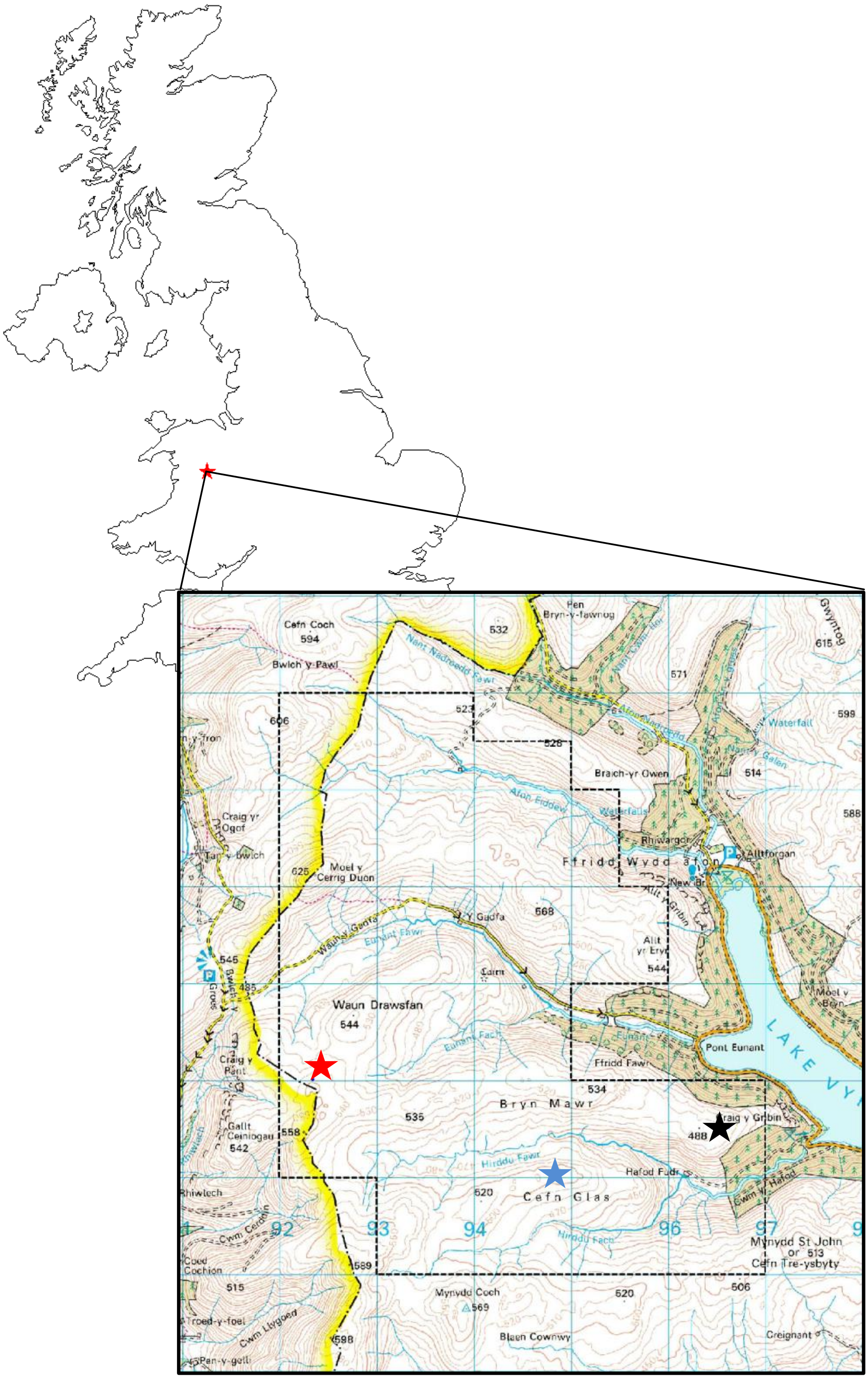

Fig. 2.1 Location of Lake Vyrnwy with three primary sites highlighted with stars: Eunant (red star, Ordnance Survey National Grid SH 92336 22015), Hafod (black, SH 96619 21523) and Hirddu (blue, SH 94839 21011). The entire study area is marked with a dashed line.

cement (Tangit PVC-U; Henkel AG & Co. KGaA, Düsseldorf, Germany) and were covered in aluminium thermal foil to reduce internal heating of the chamber from direct solar radiation.

During measurements, the collar and chambers were held together using an airtight 5 cm wide rubber band. Once sealed, CH_4 was added to a mean (±SEM) concentration of 33.3 (±1.0) ppm to enable detection of methane oxidation (Freitag *et al.* 2010) but without significantly enhancing oxidation; Saari *et al.* (2004) showed that below a level of 100 ppm, oxidation was not significantly enhanced. A retrospective study was made using a cavity-enhanced absorption technique (Hendriks *et al.* 2008) and showed no significant effect on CH_4 fluxes from the enhancement of CH_4 in the headspace (see Appendix A for details). SF_6 was also added to the headspace at the start of each measurement to a mean (±SEM) concentration of 6.18 (±0.11) ppb and, as an inert gas, was used to calculate rates of chamber leakage during the measurement period for all gases of interest (Tingey *et al.* 2000) and identify chambers which were not effectively sealed to the soil surface. Immediately following the addition of CH_4 and SF_6, five gas samples, 20 cm^3, were extracted from each chamber using a 20 cm^3 plastic syringe at recorded intervals of between 20 and 30 minutes and stored in pre-evacuated 12 cm^3 vials (Exetainer 839W, Labco Ltd, High Wycombe, UK). Mean total sampling time (±SEM) was 103 (±0.6) minutes and the actual time of any gas sample extraction was accurately recorded. Despite being purchased as pre-evacuated, all vials were evacuated until fully empty (four vials were evacuated simultaneously for 30 seconds with a 0.2 kW pump with a flow rate of 30 l min^{-1} (Type N748.4FT.18; KNF Neuberger, Freiberg, Germany)) and checked for leakage, by passing the pump exhaust through water, to ensure vials were fully evacuated and lids effectively sealed.

In order to reduce any physical disturbance of the chamber and surrounding soil during measurements, samples were taken via a 1.5 m length of vacuum tubing (Tygon Formulation R-3603 Tubing, Part number AAC00002, Saint-Gobain Performance Plastics, Akron, OH, USA), fitted to the top of the chamber through a rubber septum (SubaSeal No. 25, Sigma-Aldrich, St Louis, MO, USA) in a pre-drilled 1 cm port, and entirely sealed at the external end. Prior to extracting each sample, the air in the vacuum tubing was mixed with the chamber headspace by pumping with the syringe to ensure extraction of a well mixed sample.

Samples were analysed upon return to the lab for CH_4, CO_2 and SF_6 using a Perkin Elmer AutoSystem XL gas chromatograph (GC; PerkinElmer Instruments, Shelton, CT, USA) equipped with a 3.7 m Porapak Q 60/80 mesh column, flame ionization detector (FID) and electron capture detector (ECD). Samples were injected into the GC by an automated sampler (Biology Electronic Services, University of York, UK) and 6 port gas sampling valve (part number 610N, Arnel Inc, Parlin, NJ, USA); the over-pressurisation of vials enabled samples to automatically flow into the gas sampling valve from the automated sampler. The GC was operated at temperatures of 120 °C, 40 °C and 350 °C respectively for the injector, column and detectors; N_2 was the carrier gas, flowing at 30 mL min^{-1}. The GC was calibrated using certified standards (BOC Gases, Guildford, Surrey, UK) of 103 and 523 ppm for CH_4 and CO_2, respectively, and for SF_6, a uniform standard of 0.008 ppm was created from a single set of serial dilutions of pure SF_6 (BOC Gases) with N_2.

2.2.3 Data handling

Trace gas fluxes were calculated using the slope of linear regression between CH_4 (or CO_2) concentration and time for each individual coverbox measurement. A decision algorithm was constructed and used to objectively determine how fluxes were calculated in a manner which removed the influence of erroneous data points, corrected for headspace leakage, entirely removed a measurement or enabled further subjective examination when required. Details of the algorithm are provided in Appendix B.

The distribution of flux data within each block was checked for normality using the Kolmogorov-Smirnov test with the PROC UNIVARIATE procedure and NORMAL option on SAS® (SAS Institute Inc., Cary, NC, USA), and checked for sphericity (the equality of variance between months and vegetation types, see Field and Miles, 2010) using Mauchly's test with PROC GLM, REPEATED AND PRINTE options on SAS®. Where the assumption of sphericity was incorrect, or could not be assessed, a Greenhouse-Geisser correction was made to the degrees of freedom (Howard and Mendelssohn, 1999; Field and Miles, 2010; Kooij *et al.* 2011). The effect of vegetation type and sampling month were tested using a repeated measures ANOVA (again with the PROC GLM, REPEATED and PRINTE options on SAS®) and Duncan's *post hoc* testing (PROC GLM, MEANS and DUNCAN options on SAS®), adjusted by the Bonferroni correction (Field and Miles, 2010), for comparison of vegetation means within each sampling month. Annual flux estimations were tested for normality (PROC UNIVARIATE, as before), and for homogeneity of variance (Levene's test using PROC ANOVA, MEANS AND HOVTEST=LEVENE options on SAS®).

The extrapolation from the point measurements, which were necessarily limited both spatially and temporally, to estimating annual landscape CH_4 and CO_2 fluxes for 2009 was made using a linear interpolation between each monthly measurement to produce annual estimates for each vegetation type which were subsequently extrapolated spatially using a vegetation classification of the study site.

2.2.4 Annual landscape estimate

An annual flux and error term was produced for each vegetation type by linearly interpolating between monthly flux measurements throughout 2009. The mean flux measurement of each block (combination of site and vegetation type) was used to create a block measurement for each month. The linear interpolation was made between each block flux from December 2008 to January 2010 (PROC EXPAND procedure and METHOD=JOIN option on SAS®) and all 2009 values were summed.

In order to extrapolate the annual fluxes across the site, the proportional coverage of each vegetation type was calculated using a maximum likelihood supervised classification (Mather, 2004 pp. 221) of 1 m resolution aerial images acquired in 2006 with the IKONOS satellite (made available by the Countryside Council of Wales, MacBean personal communication), and using ENVI 4.6.1 image processing software (ITT Visual Information Solutions, Bracknall, Berkshire, UK). The high spatial resolution and multispectral IKONOS images have been shown to produce highly accurate vegetation classifications in a variety of landscapes, including the UK uplands (Belluco *et al.* 2006; Carleer and Wolff, 2004; Mehner *et al.* 2004). Reference data, which consisted of identified examples of each vegetation type, were collected using a differential GPS (MobileMapper CX, Ashtech S.A.S., Carquefou, France) across the site, taking into account aspect and elevation to account for varying illumination. The initial classification used 75% of the reference data as training data, whilst the remaining 25% were used as validation data for *post hoc* accuracy testing of the classification by calculating the probability of a pixel being correctly classified (%). Once proportional values had been calculated for each class, the mean of each vegetation type were appropriately weighted and combined to give a single landscape mean (μ_l) using:

$$\mu_l = \frac{1}{100}\left(\sum_i (R_i F_i)\right) \qquad (2.1)$$

where R_i is the proportional coverage (%) of each vegetation type i and F_i is the mean flux of each vegetation type i. A single landscape standard deviation (σ_l) was also calculated by weighting and combining the standard deviation of each vegetation type as follows:

$$\sigma_l = \sqrt{\frac{1}{99}\left(\sum_i \left[(R_i - 1)\sigma_i^2 + \left(R_i F_i^2\right)\right] - \left(100 \times F_i^2\right)\right)} \tag{2.2}$$

where σ_i is the standard deviation of each vegetation type i.

In order to incorporate the error term of the vegetation classification (probability of incorrect classification) into the landscape estimate, the accuracy term was used to adjust the proportional coverage to represent a range of scenarios (following methods from Bubier *et al.* 2005). Specifically, to estimate the highest landscape flux, the proportional coverage (%) of the strongest emitting class (C_s) was increased by the largest estimated error as follows:

$$C_s = C_{is} \cdot \left[\left(\frac{A}{\sum_v C_v}\right) + \left(\sum_v C_v - A\right)\right] \tag{2.3}$$

where C_{is} is the initial coverage estimate (%) for the strongest emitting class, A is the probability of a pixel being correctly classified (%) and C_v is the initial coverage estimate for each vegetation class, and the proportional coverage (%) of all other classes (C_o) is reduced as follows:

$$C_o = C_{io} \cdot \left(\frac{A}{\sum_v C_v}\right) \tag{2.4}$$

where C_{io} is the initial coverage estimate (%) of each of the other classes. The lowest landscape flux was estimated in a similar manner, where the proportional coverage of the weakest emitting vegetation class was increased using Equation (2.3), whilst the other classes were reduced using Equation (2.4).

2.3 Results

2.3.1 Flux measurements

Out of a total of 829 measurements made at the field site, 556 CH_4 fluxes were accepted by the decision algorithm (see Appendix B), ranging from -2.14 to 18.21 mg CH_4 m^{-2} h^{-1} for grass, -1.71 to 4.56 mg CH_4 m^{-2} h^{-1} for heather, -2.62 to 17.95 mg CH_4 m^{-2} h^{-1} for Juncus and -2.67 to 15.35 mg CH_4 m^{-2} h^{-1} for sedge. In addition, 574 CO_2 fluxes were measured, ranging from 0 to 1596.4 mg CO_2 m^{-2} h^{-1} for grass, 0 to 723.2 mg CO_2 m^{-2} h^{-1} for heather, 0 to 3136.5 mg CO_2 m^{-2} h^{-1} for Juncus and 0 to 2924.7 mg CO_2 m^{-2} h^{-1} for sedge.

Mean monthly CH_4 fluxes for each vegetation type during 2009, calculated from block measurements, show a distinct seasonal pattern. Fluxes remained close to zero, with some net CH_4 oxidiation, during the first five months of 2009 followed by peak fluxes (net emission of CH_4) in June, which continued until the end of 2009 (Fig. 2.2). Sedge was a particularly strong source of CH_4 even in December. The one vegetation type which displayed an exception to this pattern was heather which changed from a consistent small source of CH_4 to a small sink from March to June. A large amount of variation in CH_4 fluxes between measurement sites is apparent, but sphericity was not testable due to insufficient degrees of freedom. The assumption that sphericity had been violated, and subsequent adjustment of degrees of freedom ($\hat{\varepsilon} = 0.1285$), resulted in no significant overall effect of vegetation type ($p = 0.153$), no significant overall effect of sampling month on CH_4 fluxes ($p = 0.103$) and no interaction between vegetation type and time of sampling ($p = 0.319$). Mean monthly CO_2 fluxes also showed a seasonal pattern with some similarities: a large increase in respiration followed low fluxes at the start of the year, and a slower decline in activity in the second half of the year. However, differences in the timing of peak fluxes for CH_4 and CO_2 are evident as the highest respiration occurred in May and June for all vegetation types (Fig. 2.3) as opposed to between July and October for CH_4 fluxes. After

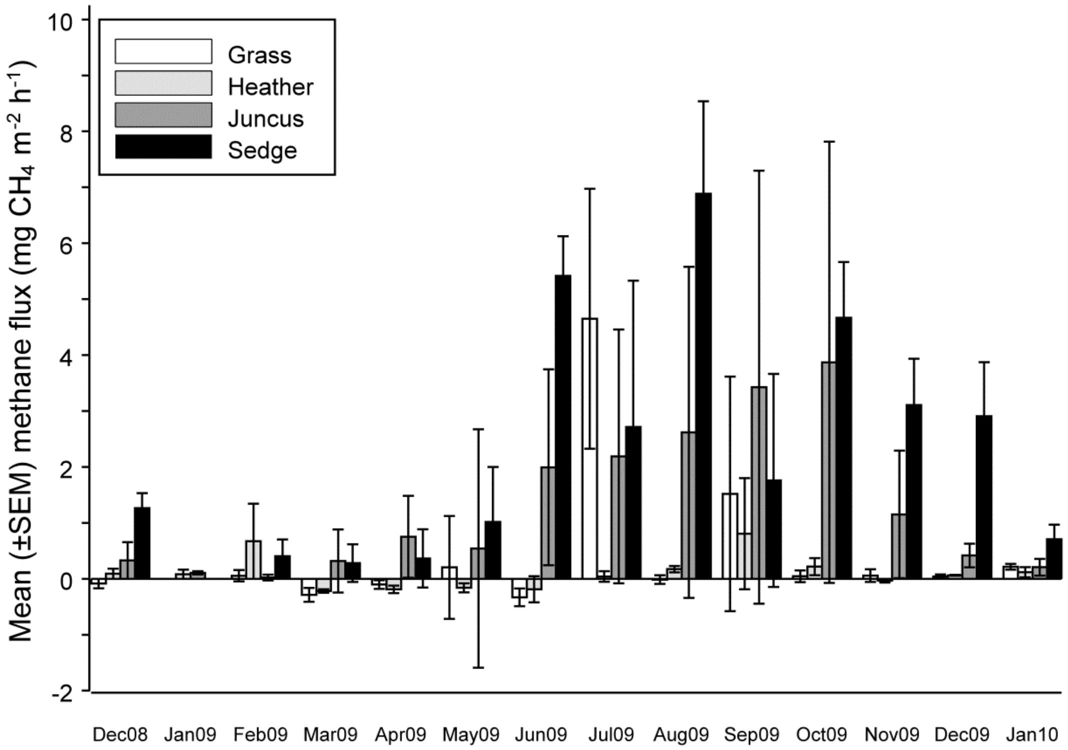

Fig. 2.2 Mean (± SEM) CH_4 flux measurement (mg CH_4 m^{-2} h^{-1}) of each vegetation type during each sampling event from December 2008 to January 2010. There is no significant effect of vegetation (p = 0.153), of sampling month (p = 0.103) or of interaction between vegetation and sampling month (p = 0.319), n = 3.

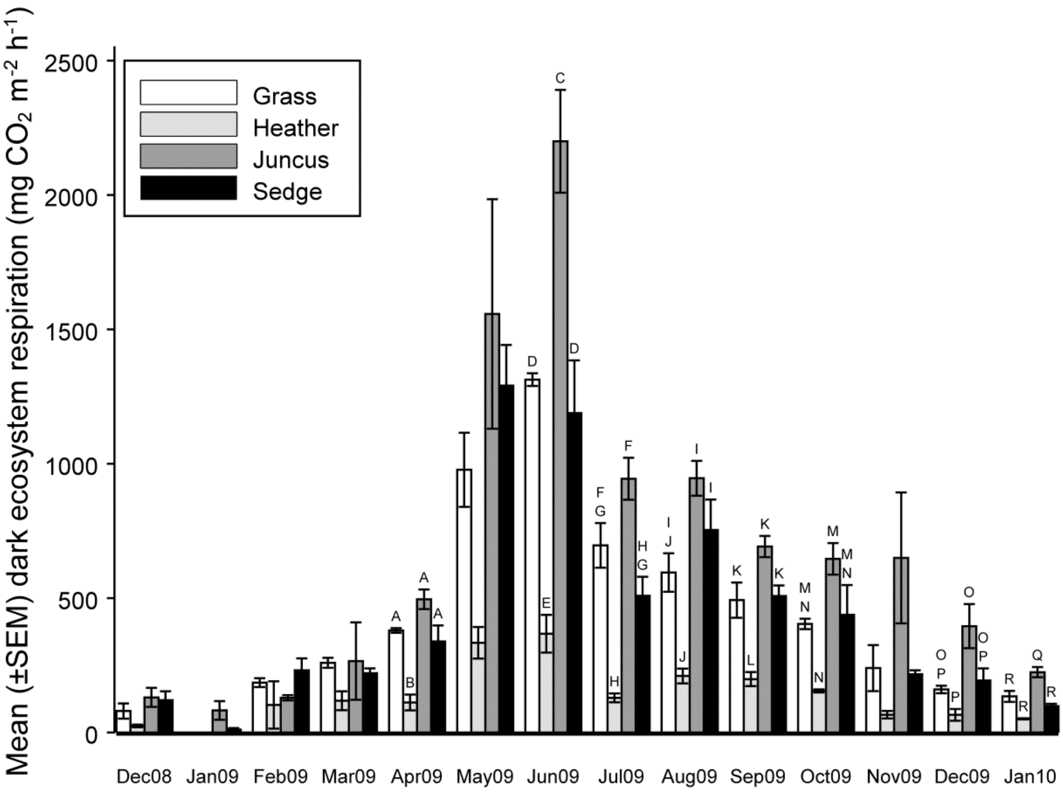

Fig. 2.3 Mean (± SEM) dark ecosystem respiration measurement (mg CO_2 m^{-2} h^{-1}) of each vegetation type during each sampling event from December 2008 to January 2010. There is a significant effect of vegetation ($p < 0.001$), sampling month ($p < 0.001$), and of interaction between vegetation and sampling month ($p = 0.002$). Within each sampling month, vegetation types with the same letters are not significantly different from each other (*post hoc* Duncan's test with a Bonferroni correction of significant p-value of 0.004), n = 3.

making a similar correction for lack of sphericity as for the methane data ($\hat{\varepsilon} = 0.1516$), there was a significant overall effect of vegetation type on CO_2 fluxes ($p < 0.001$), a significant overall effect of sampling month on CO_2 fluxes ($p < 0.001$) and a significant interaction between vegetation type and time of sampling ($p = 0.002$). *Post hoc* testing within each month showed significant effects ($p < 0.004$) of vegetation type during April 2009, June 2009 until October 2009, December 2009 and January 2010 as illustrated in Fig. 2.3.

2.3.2 Annual landscape estimate

The estimation of an annual landscape CH_4 flux was calculated from the estimates of annual CH_4 fluxes for each vegetation type, using linear interpolation between monthly measurements (Fig. 2.4). These estimates suggest that each vegetation type was a source of emission during the measurement period. The apparent difference in variance between each vegetation type, specifically the large variation in estimates for Juncus compared to the smaller variation in grass and heather estimates, was not significant. The annual CH_4 emission from sedge (annual mean (±SEM) estimate of 19.9 (±5.1) g CH_4 m^{-2} $year^{-1}$) and Juncus (12.0 (±11.5) g CH_4 m^{-2} $year^{-1}$) appeared higher than from grass (3.6 (±1.0) g CH_4 m^{-2} $year^{-1}$) or heather (1.0 (±0.7) g CH_4 m^{-2} $year^{-1}$) but differences were not significant ($p = 0.217$).

An estimate of annual dark ecosystem respiration at the landscape scale was similarly based on annual respiration estimates for each vegetation type (Fig. 2.5). A significant effect of vegetation type on respiration was observed ($p < 0.001$) with *post hoc* Duncan's showing that Juncus (annual mean (±SEM) estimate of 6.4 (±0.5) kg CO_2 m^{-2} $year^{-1}$) was significantly higher than all other vegetation types, heather (1.4 (±0.3) kg CO_2 m^{-2} $year^{-1}$) was significantly lower than all other vegetation types, and there was no significant difference between grass (4.1 (±0.1) kg CO_2 m^{-2} $year^{-1}$) and sedge (4.2 (±0.5) kg CO_2 m^{-2} $year^{-1}$).

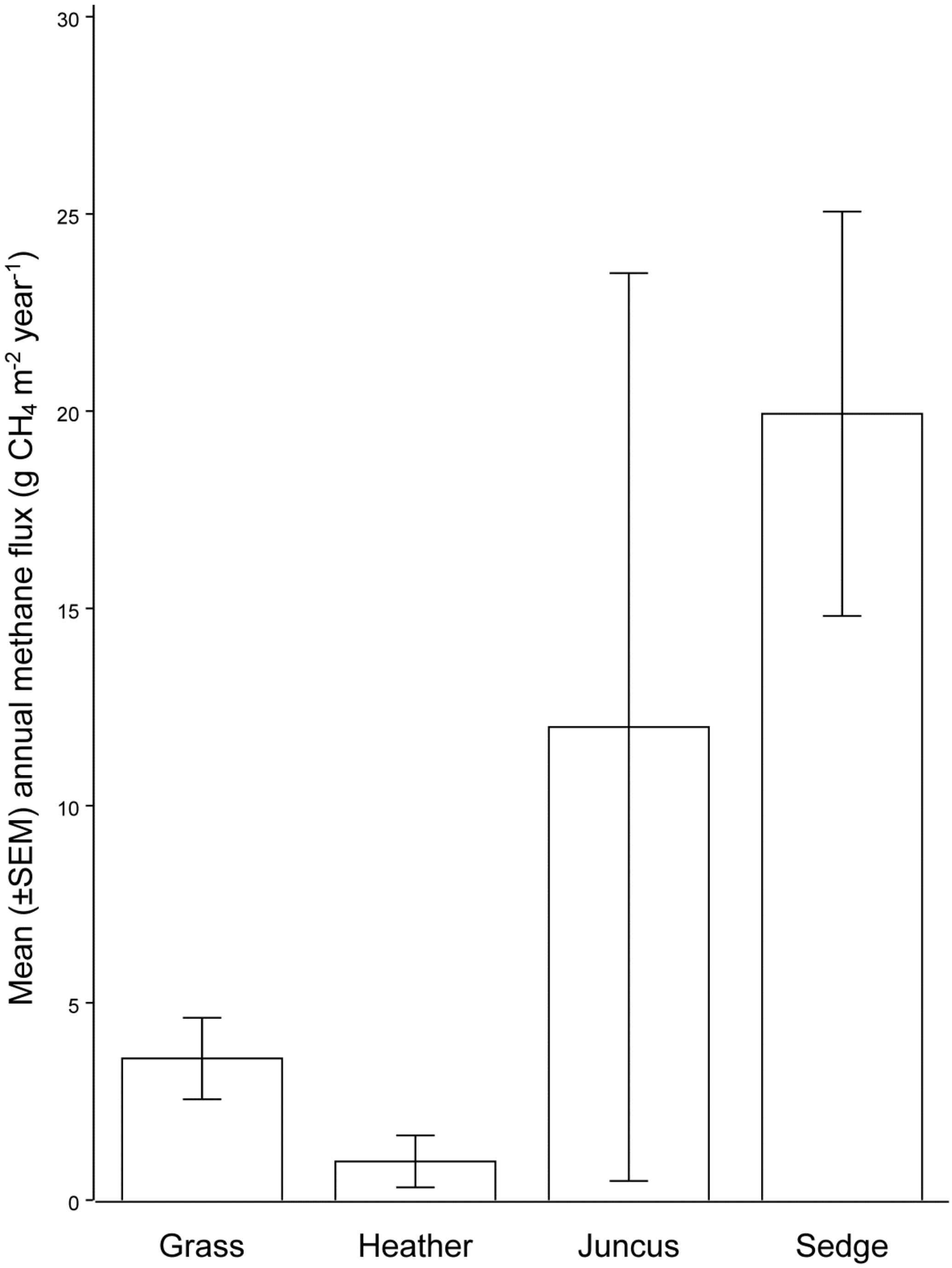

Fig. 2.4 Mean (± SEM) annual estimation of CH_4 flux (g CH_4 m^{-2} $year^{-1}$) for each vegetation type. There is no significant effect of vegetation on methane flux ($F(3,8) = 1.85$, $p = 0.217$), $n = 3$.

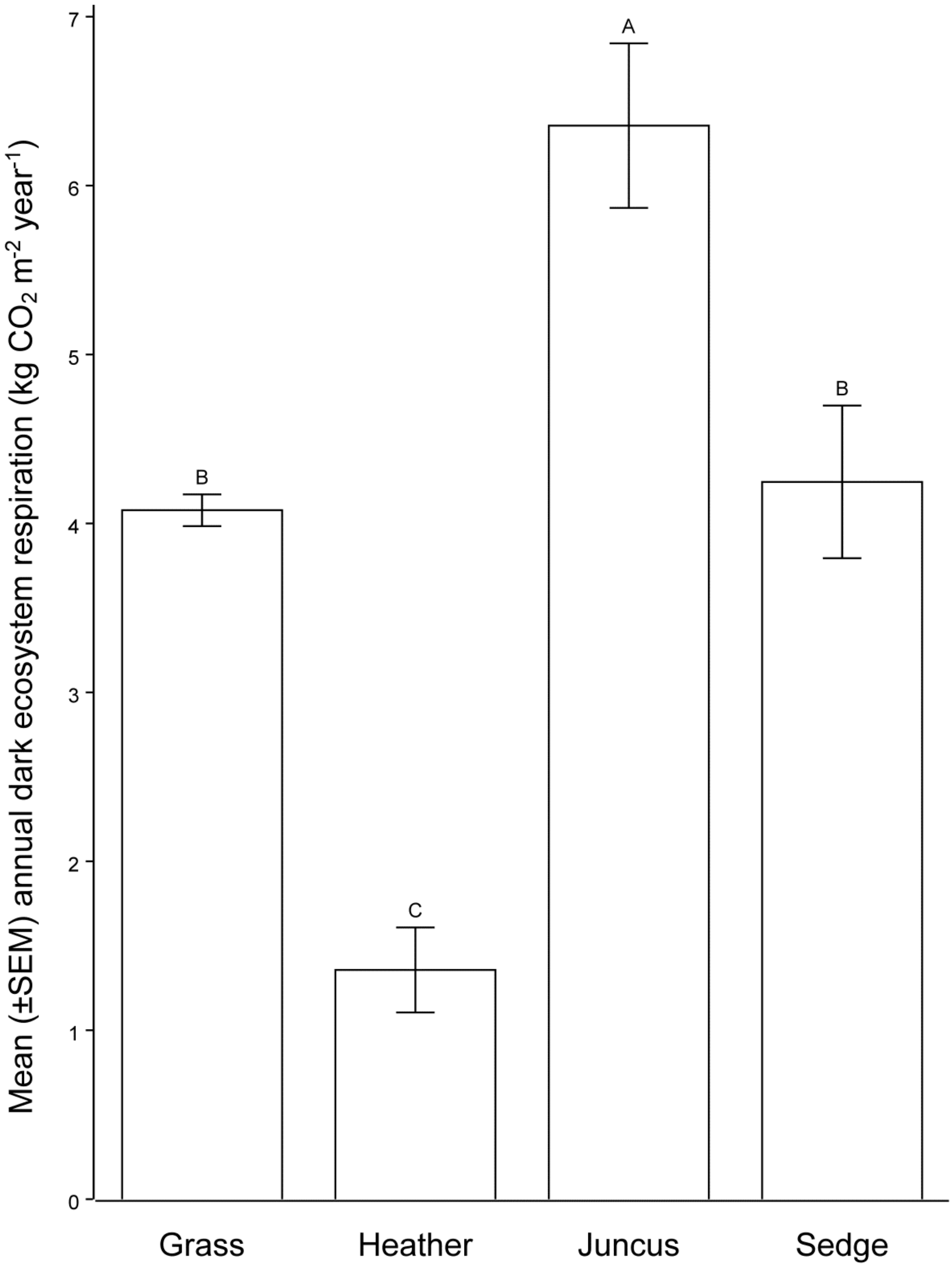

Fig. 2.5 Mean (± SEM) annual estimation of dark ecosystem respiration (kg CO_2 m^{-2} $year^{-1}$) for each vegetation type. There is a significant effect of vegetation on respiration ($F(3,8) = 32.70$, $p = 0.000771$); vegetation types with the same letters are not significantly different from each other (*post hoc* Duncan's test), n = 3.

The initial red, green and blue IKONOS scene (Fig. 2.6) was used to produce the vegetation classification shown in Fig. 2.7. The validation data showed the accuracy of the classification (probability of a pixel being correctly classified) to be 72.2%. The proportional coverage of each vegetation type was calculated as 3.4%, 34.3%, 17.9% and 27.8% for grass, heather, Juncus and sedge, respectively, with heather dominating the tops of ridges and some North-facing slopes. In addition to the four identified classes of vegetation type, an additional unclassified category was produced containing pixels which were not allocated to a trained class (covering 6.2% of the study area) and pixels belonging to groups excluded from the study: road surface (1.2%), bracken dominated vegetation (5.0%), and forested areas (4.2%). By comparison with the initial scene, or from prior knowledge of the site, it is clear that the classification had correctly placed areas covered by cloud in the unclassified class (for example Fig. 2.8), but had misclassified areas of forest as heather (for example, the Southern section of forest in the South-Eastern corner of the scene; Fig. 2.7); an error which was likely to have reduced the landscape estimate of both CH_4 flux and respiration as heather had the lowest mean flux measurements. In contrast, the classification was unable to recognise all patches of mown heather (for example Fig. 2.9) which was likely to have increased both landscape estimates for the opposing reason.

Final landscape estimates, shown in Table 2.1, include the best estimate (±SEM) of annual landscape flux for methane, 9.8 (±3.8) g CH_4 m^{-2} $year^{-1}$, and for respiration, 3.5 (±0.6) kg CO_2 m^{-2} $year^{-1}$. Using IPCC estimates of the Global Warming Potential (GWP) for CH_4 over a 100 year period (Forster *et al.* 2007), the annual landscape flux for methane is 0.24 (±0.10) kg $CO_2^{equivalent}$ m^{-2} $year^{-1}$. Also shown is the influence on these best estimates of the most extreme influence of the 72.2% accuracy in the vegetation classification. With regards to annual landscape estimates of methane flux, the assumption that all misclassified pixels could have been classified as the weakest emitter, heather, resulted in an increased proportional coverage of heather to 40.9%, and the lowest estimate of

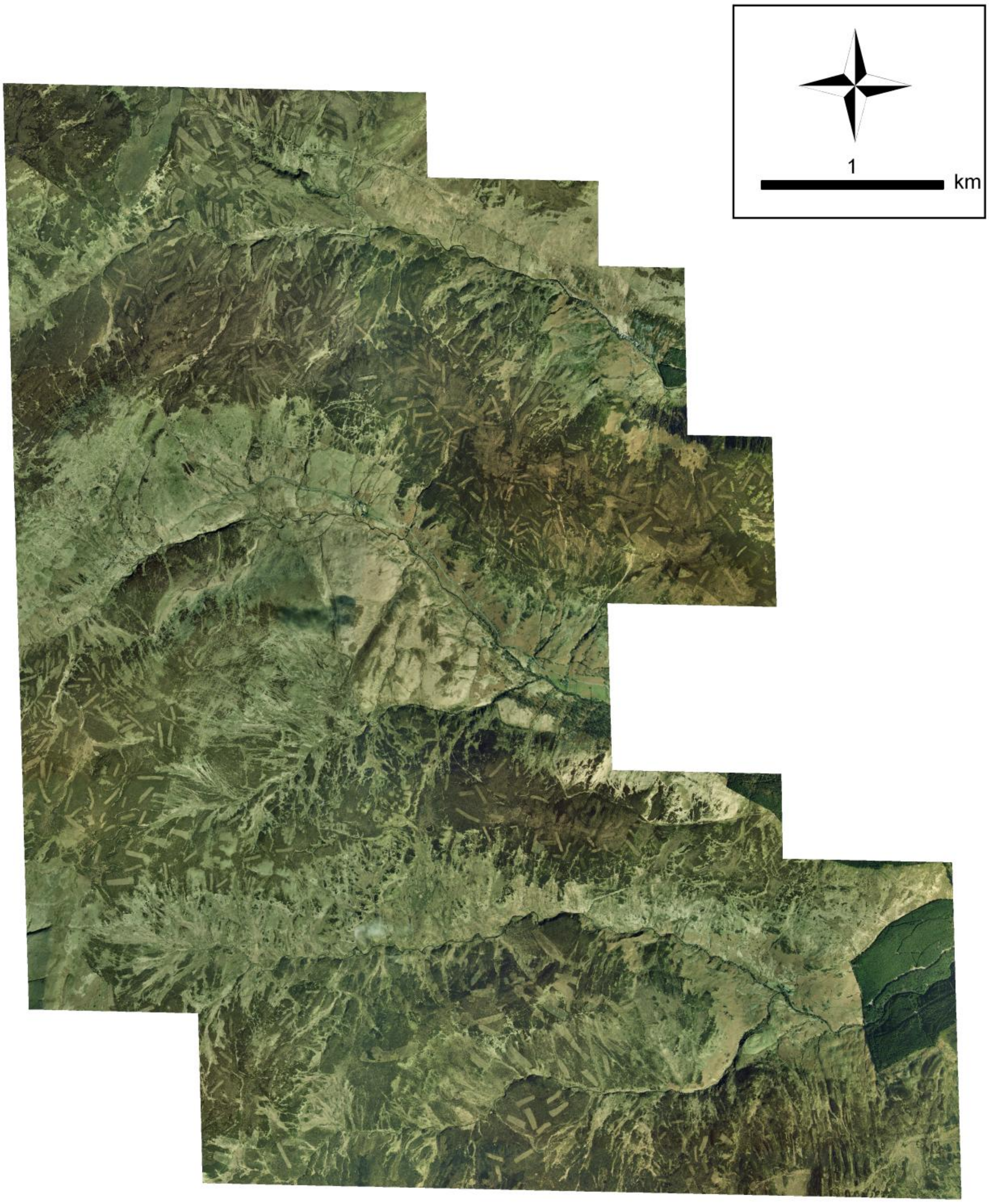

Fig. 2.6 Original IKONOS image (aerial photo) of the study area taken in 2006. The resolution of the image is a 1 x 1 m pixel size and the image relates directly to the study area marked on the 1 km grid of Fig. 2.1.

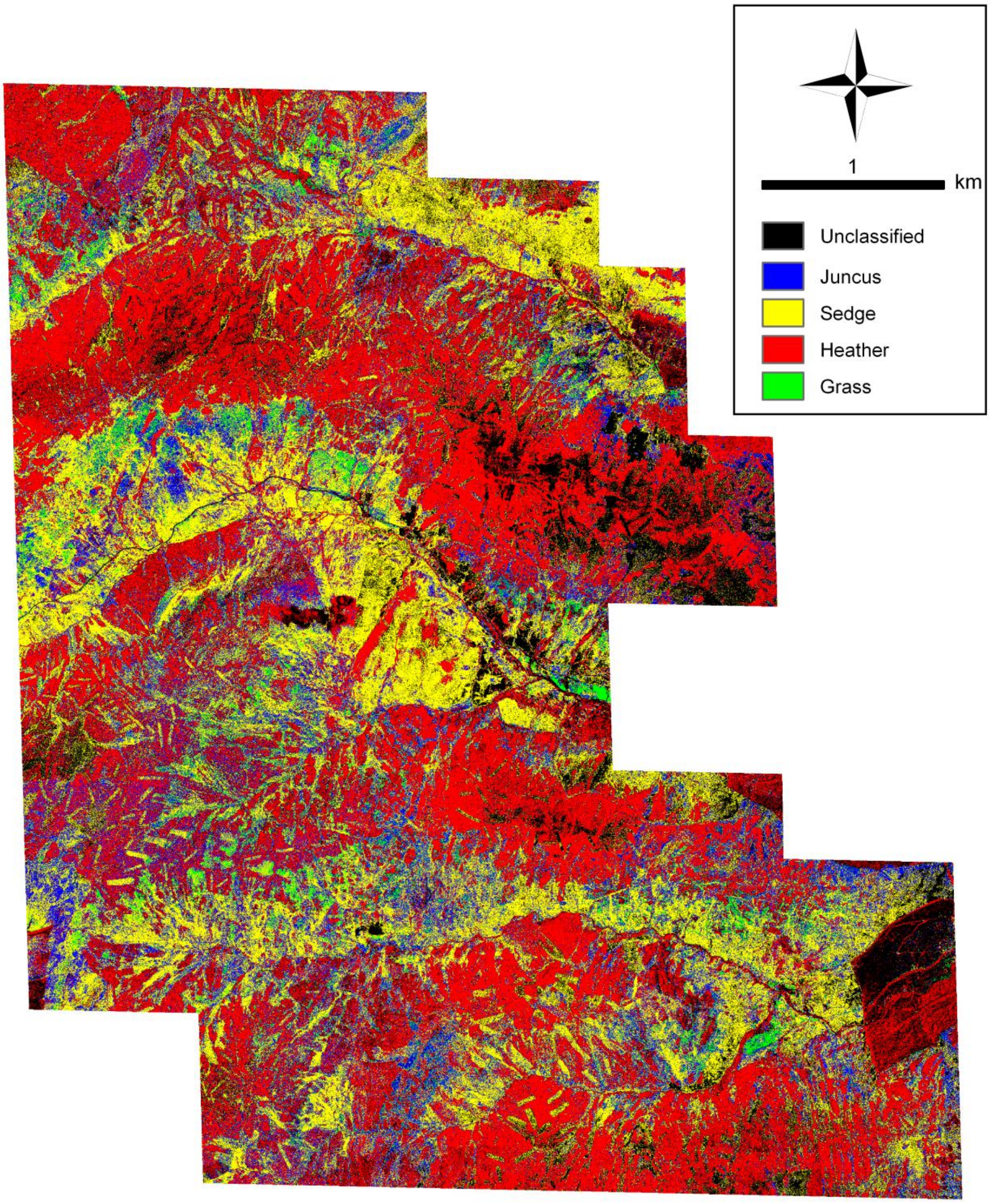

Fig. 2.7 Vegetation classification of the entire study area based on the IKONOS image in Fig. 2.6. The resolution of the image is a 1 x 1 m pixel size. The legend relates to the four supervised vegetation classes and an unclassified class, consisting of unidentifiable pixels and excluded pixels containing roads, forest and bracken.

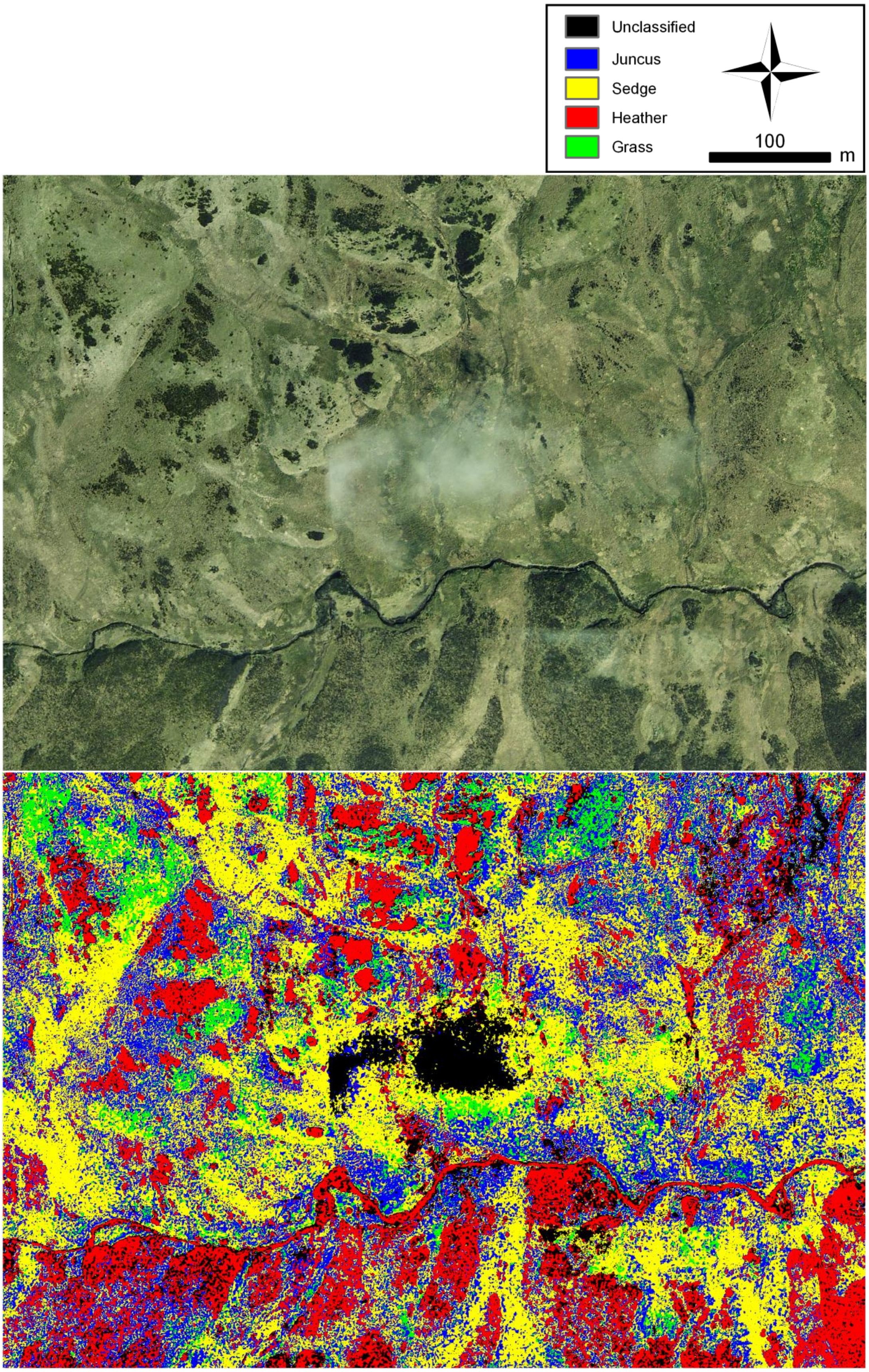

Fig. 2.8 Contrast of aerial photo and classification showing clouded areas as unclassified. Both images are centred around SH 93892 21368 and cover an area of 500 m by 725 m.

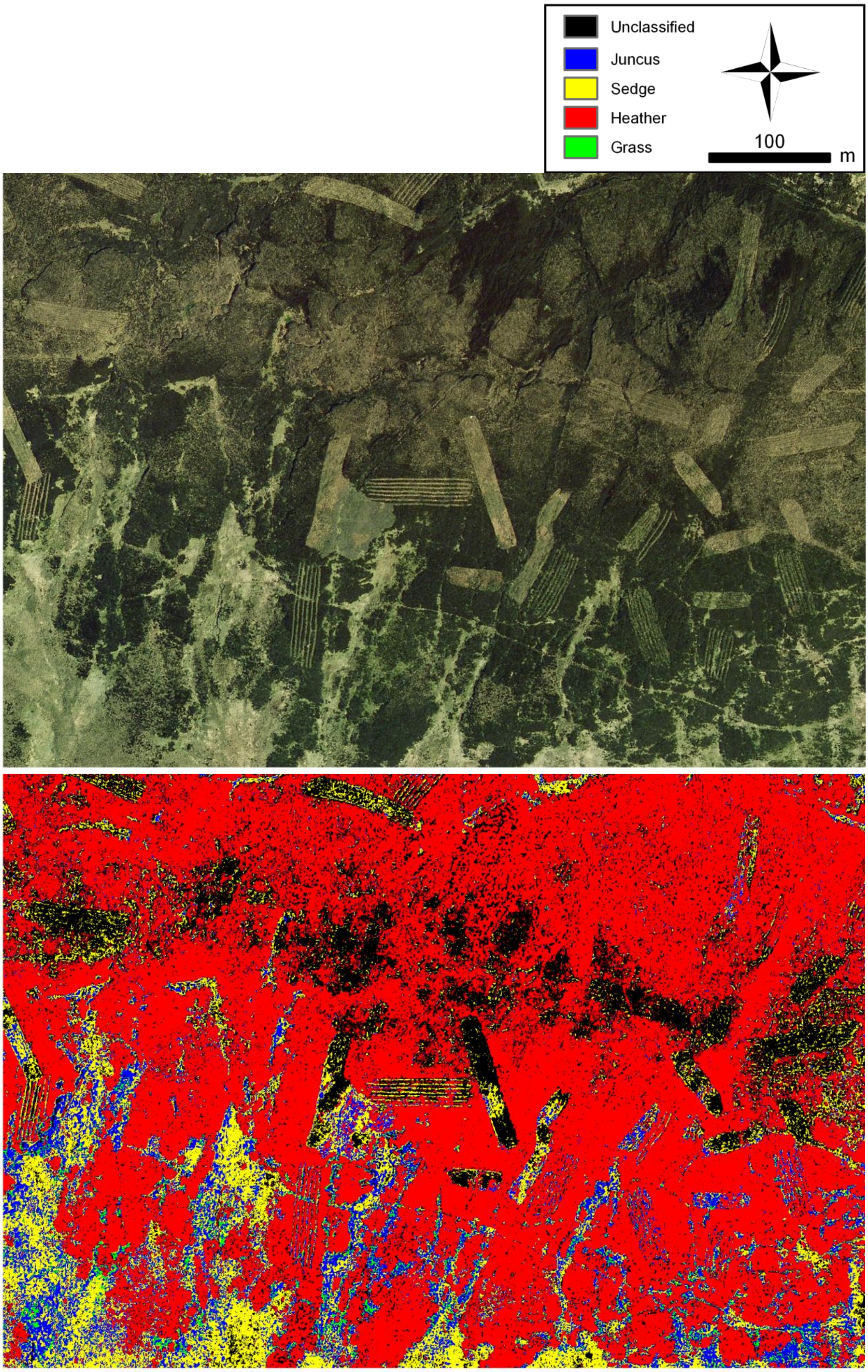

Fig. 2.9 Contrast of aerial photo and classification showing mown heather as unclassified. Both images are centred around SH 94865 21858 and cover an area of 500 m by 725 m.

Table 2.1 Impact of vegetation classification errors on annual landscape estimates of CH_4 and CO_2 fluxes. Different methods of estimating the proportional coverage of each vegetation class provide (i) the best estimate and (ii) a wider range of estimates for landscape fluxes.

Estimate	Proportional coverage (%)				Annual landscape flux (±SEM)	
	Grass	Heather	Juncus	Sedge	Methane ($g\ CH_4\ m^{-2}\ year^{-1}$)	Respiration ($kg\ CO_2\ m^{-2}\ year^{-1}$)
Best	3.4	34.3	17.9	27.8	9.8 (±3.8)	3.5 (±0.6)
Lowest CH_4	3.0	40.9	15.5	24.1	8.6 (±3.7)	
Highest CH_4	3.0	29.7	15.5	35.3	11.1 (±3.8)	
Lowest CO_2	3.0	40.9	15.5	24.1		3.2 (±0.6)
Highest CO_2	3.0	29.7	26.7	24.1		3.9 (±0.6)

of 8.6 (±3.7) g CH_4 m^{-2} $year^{-1}$. In contrast, the assumption that all misclassified pixels could have been the strongest emitter, sedge, resulted in an increase of proportional coverage of sedge to 35.3%, and the highest estimate of 11.1 (±3.8) g CH_4 m^{-2} $year^{-1}$. Similarly, the lowest annual landscape estimate for respiration of 3.2 kg CO_2 m^{-2} $year^{-1}$ resulted from increasing the proportional coverage of heather, and the largest annual landscape estimate for respiration of 3.9 (±0.6) kg CO_2 m^{-2} $year^{-1}$ resulted from increasing the proportional coverage of Juncus to 26.7%.

2.4 Discussion

2.4.1 Seasonal CH_4 measurements

Very few studies of CH_4 fluxes from upland blanket bogs in the UK which include flux measurements made across all seasons have been performed or published and it appears that Ward *et al.* (2007) have made and presented the only previous complete series of annual measurements from an upland blanket bog in the UK. Others who have made measurements in similar conditions, including raised bogs in the lowlands of the UK and flushed gully mires, include: Clymo and Pearce (1995), who combined measurements from a raised bog over a 30 month period and presented them as a single annual pattern; Baird *et al.* (2010) and Dinsmore *et al.* (2009a), who also made regular field measurements in raised bogs for 10 and 19 months, respectively; and Hughes *et al.* (1999), who present fortnightly measurements over a six year period from a flushed gully mire. Most published studies only sample during summer months (for example Fowler *et al.* 1995a; McNamara *et al.* 2008), or are reliant on modelled fluxes which are uncalibrated for a specific site or time period (Worrall *et al.* 2003; Worrall *et al.* 2007b; Worrall *et al.* 2009). Whilst not primarily aiming to provide annual estimates, the period typically excluded from typical peatland studies (Fowler *et al.* 1995a; Saarnio *et al.* 1997; Bubier *et al.* 2005; McNamara *et al.* 2008) includes the first four to five months of the year, which during 2009 at the current study site exhibited relatively low fluxes, and the last three to five months of the year, which displayed an extended shoulder of activity from the sedge and heather vegetation types.

The impact of excluding entire seasons from studies which aim to construct representative annual estimates of fluxes include: (i) the systematic biasing of measurements, in this case, the exclusion of non-summer fluxes may have biased a seasonal estimate towards higher CH_4 fluxes; (ii) limiting the range of environmental conditions over which measurements are made, subsequently constraining the scope of model extrapolation; and (iii) the possibility of missing key seasonal events. This final point was clearly demonstrated by Mastepanov *et al.* (2008) in an Arctic study which revealed that the CH_4 flux during a three week post-growing season period was equal to the combined flux during the entire summer growing period. Extreme winter conditions and significant periods of permafrost and snow cover provide practical and scientific reasons why full annual measurements are rare in Arctic and Boreal based studies (Jackowicz-Korczynski *et al.* 2010), but such constraints are less justifiable for restricting the sampling strategy of UK-based seasonal studies.

2.4.2 Seasonal flux patterns

The seasonal pattern of CH_4 fluxes from the current study (Fig. 2.2), with low CH_4 fluxes and some net CH_4 oxidation during first five months of 2009 followed by rapid increase in activity and longer decline of activity to the end of the year is, surprisingly, *not* unique. Annual measurements from other areas of blanket bog include an upland site in Northern England (Ward *et al.* 2007) where emissions of CH_4 during 2003 peaked in August, but the following year, emissions peaked in September (when unfortunately, measurements ceased). Ward *et al.* (2007) concluded that the seasonal pattern observed follows the seasonal pattern of temperature (air temperature showed a significant correlation with CH_4 fluxes, r^2 of 0.280). However, examination of the data reveals that higher CH_4 fluxes were maintained throughout the autumn period of 2003, with mean fluxes in November still being higher than in June of the same year. Results from non-upland blanket bog sites, such as a raised bog in Wales (see Fig. 4 in Baird *et al.* 2010) and a mid-boreal mire in Northern Europe (see Fig. 1 in Leppala *et al.* 2011), also showed similar late-summer peaks and a steady decline through autumn. One of the longest set of measurements (bi-weekly CH_4 flux measurements over a six year period) were made at a flushed gully mire, also in Wales, and showed a similar slow autumnal decline, with fluxes not returning to low spring levels until after the end of each calendar year (see Fig. 3 in Hughes *et al.* 1999). The discrepancy between this observed seasonal pattern and models of CH_4 fluxes which are based on temperature and show a quicker autumnal decline (e.g. Fig. 1a of Ginzburg *et al.* 2011) may have meant the consistently observed ‘late-autumn shoulder’ of atmospheric CH_4 concentration in the Northern hemisphere remained unexplained (Dlugokencky *et al.* 1994). With the exception of higher fluxes in May and June, dark ecosystem respiration at the current site showed a more typical seasonal pattern (Fig. 2.3) which is also seen at other blanket bog sites (Ward *et al.* 2007). The Juncus vegetation type showed some maintenance of higher respiration fluxes throughout autumn, but not as distinctive as it was for the CH_4 fluxes.

Environmental controls on CH_4 fluxes at Lake Vyrnwy are discussed in detail in Chapter 3 but if CH_4 fluxes consistently peak later in the year than do maximum temperatures or incoming solar radiation, and exhibit a late-autumn shoulder of activity then any hypothesis must explain both these factors. Fenner *et al.* (2005) showed that the thermal response of various carbon-cycling enzymes altered according to seasonality which, if also applicable to methantrophy or methanogenesis, may explain a delayed response to temperature or radiation through seasonal acclimation. The late-autumn shoulder of activity, and contrasting rapid increase of activity during early-summer, could be produced by differing speed of response to two or more environmental variables, or by the differing speed of response by populations of methanogens and methanotrophs. Differing responses by methanogen and methantroph populations are suggested by MacDondald *et al.* (1998) as the reason for conflicting responses to temperature that they observe at different times of the season. They conducted a semi-seasonal study of CH_4 fluxes from monoliths extracted from a blanket bog and generally observe a positive response of CH_4 flux to temperature, however a negative response was seen when peat temperatures were decreasing in late summer. Flux measurements from a replicated manipulation of water table on peat monoliths, extracted from the same Lake Vyrnwy site used in the current study, showed a marked delayed response of net CH_4 flux of four months to experimental lowering of the water table (Lukac *et al.* personal communication) suggesting delayed responses may not only occur in response to temperature and radiation. Observations of the seasonal acclimation of soil CH_4 processes to changes in environmental conditions are not common. However, an inter-annual study by Hughes *et al.* (1999) showed that, after experimental simulation of a moderate summer drought and subsequent reduction in CH_4 emissions, the CH_4 flux returned to higher control emissions within three years.

2.4.3 Effect of vegetation on CH_4 fluxes

In contrast to theoretical reasons (Le Mer and Roger, 2001; Philippot *et al.* 2009) and empirical evidence (Frenzel and Rudolph, 1998; Bellisario *et al.* 1999; Greenup *et al.* 2000) supporting the importance of vegetation type in controlling CH_4 fluxes, there was no significant effect of vegetation on CH_4 fluxes in the current study. It was felt that the apparent difference in flux means, and the potential impact on the annual landscape estimate, meant stratification by vegetation type was justified and the lack of significant difference was influenced by the large spatial variability of flux measurements in relation to the small number of replicates. As the most variable of vegetation types, the fluxes from Juncus were possibly not representative of similar areas across the site. Sampling in the current study was spatially biased towards the top of ridges; these sites were selected so that all flux measurements could be associated with measurements from meteorological stations (see Chapter 3) which were sited on ridges to enable remote interrogation and for use by other users of the scientific 'platform' at Lake Vyrnwy. This was an unusual location for areas dominated by *Juncus* species which are more typically associated with wet areas around water courses (as seen in Fig. 2.8) and higher CH_4 fluxes (Roura-Carol and Freeman, 1999). Consequently, the estimates of annual landscape CH_4 flux presented here are likely to be conservative. This could be rectified with wider spatial sampling to incorporate topographical variation across the site (such as hydrological heterogeneity), or by the inclusion of key environmental conditions (such as water table) in the models used to extrapolate CH_4 fluxes. For example, the construction of regression models between CH_4 fluxes and environmental conditions (as in Chapter 3) can be used as a basis for spatial extrapolation, rather than just using vegetation coverage. Without any stratification, the annual landscape estimate of CH_4 flux was not greatly altered by removing the vegetation stratification; estimates were reduced to 9.1 (3.5) g CH_4 m^{-2} $year^{-1}$ from a stratified estimate of 9.8 (3.8) g CH_4 m^{-2} $year^{-1}$, primarily due to the increased contribution of the grass vegetation type (which in effect increased from a proportional coverage of 3.4% to 25%) but this influence was not greater due to the corresponding decreased contribution of the heather vegetation type (from 34.3% to 25%), the lowest emitter of CH_4.

2.4.4 Annual landscape estimate

All estimates of annual landscape CH_4 flux in the current study, including the most extreme possibilities potentially resulting from misclassification, suggest that the blanket bog around Lake Vyrnwy is a net source of CH_4. In comparison to other estimates of UK blanket bog, the best estimate (±SEM) of 9.8 (±3.8) g CH_4 m^{-2} $year^{-1}$ at this site sits between the 2.1 g CH_4 m^{-2} $year^{-1}$ estimate made at Loch More, Caithness by Fowler *et al.* (1995b) and the 17.2 g CH_4 m^{-2} $year^{-1}$ at Moor House, North Pennines by McNamara *et al.* (2008). Both these estimates were extrapolated from measurements taken between May and June and neither provided an error term on the final estimate, but they do differ in method of measurement; eddy covariance technique was used at Loch More and non-steady state chambers were used at Moor House. The only study that measured CH_4 fluxes throughout the year at an upland blanket bog Ward *et al.* (2007) did not produce a landscape estimate but other estimates have been made for a variety of northern peatlands in Europe and North America. Dinsmore *et al.* (2009a) estimated an annual flux of ca. 0.1 g CH_4 m^{-2} $year^{-1}$ for a low-lying peat bog using a simple non-stratified method of extrapolation, whilst Drewer *et al.* (2010) produced marginally higher annual estimates of between 0.2 and 0.5 g CH_4 m^{-2} $year^{-1}$ for the same site and period. Clymo and Pearce (1995) estimated an annual flux of 4.3 g CH_4 m^{-2} $year^{-1}$ for a raised bog in the UK, and higher estimates of 5.1 and 8.3 g CH_4 m^{-2} $year^{-1}$ for two separate snow-free seasons were obtained from a mixture of bogs and fens in North America by Bubier *et al.* (2005). Higher still are the estimates of 27.3 g CH_4 m^{-2} $year^{-1}$ from a fen site in Fennoscandia (Saarnio *et al.* 1997), 17 and 23 g CH_4 m^{-2} $year^{-1}$ for two years from another fen site in northern Europe (Drewer *et al.* 2010). and of between 8.1 and 19.1 g CH_4 m^{-2} $year^{-1}$ from fens in a variety of successional states during the snow free period (Leppala *et al.* 2011). In this context, the fluxes from the blanket bog around Lake Vyrnwy are higher than most other peatland sites and years in the UK, but lower than the CH_4 emissions from more nutrient rich fens in arctic and sub-arctic locations.

The annual landscape estimate of ecosystem respiration at Vyrnwy (3.5(±0.6) g CH_4 m^{-2} $year^{-1}$) is lower than the mean summer maximum at a blanket bog in Northern England (6.5 kg m^{-2} $year^{-1}$ by Ward *et al.* 2007) and higher than the mean night-time respiration from a blanket bog in Scotland (0.8 kg m^{-2} $year^{-1}$ from Fowler *et al.* 1995a). McNamara *et al.* (2008) estimated an annual landscape flux of respiration at Moor House of 1.4 kg CO_2 m^{-2} $year^{-1}$ with a combined Global Warming Potential (GWP) for CH_4 and ecosystem respiration of 1.8 kg $CO_2^{equivalent}$ m^{-2} $year^{-1}$. This combined GWP at Moor House falls below the error term of GWP at Vyrnwy (3.8 (0.7) kg $CO_2^{equivalent}$ m^{-2} $year^{-1}$), but the relative contribution of CH_4 at Moor House (22.3% of GWP) is much higher than for Lake Vyrnwy (6.5% of GWP). Whilst the focus of the current study was primarily CH_4 fluxes, it would initially appear that, when considering relative contribution to GWP, CH_4 fluxes are of much less importance than for CO_2. However, as photosynthesis was not measured the net exchange of carbon between terrestrial and atmospheric pools cannot be identified. Ward *et al.* (2007) showed that, throughout the year, photosynthesis at an upland blanket bog in Northern England remained in equilibrium with respiration, with the exception of the summer period when the site became a net sink for CO_2. A similar balance between respiration and photosynthesis at Lake Vyrnwy would reduce overall GWP and increase the relative importance of the CH_4 fluxes. The relative amount of different GHGs is important when considering ecosystem responses to some types of land management and to future changes in climate. For example, artificially draining peatlands would be expected to decrease CH_4 fluxes and increase respiration (Strack and Waddington, 2007; Dinsmore *et al.* 2009b); whilst projected increases in temperature and alteration to monthly rainfall due to climate change have been projected to increase both CH_4 flux and soil respiration (Worrall *et al.* 2007b).

2.4.5 Annual landscape flux error term

Of the annual landscape estimates mentioned in Section 2.4.4, most did not include an error term. Only Bubier *et al.* (2005) and Dinsmore *et al.* (2009a) indicated any more than a single value when providing a landscape estimate. For studies which extrapolate spatially using stratified measurements and remotely-sensed landscape images (such as Saarnio *et al.* 1997; McNamara *et al.* 2008; Forbrich *et al.* 2011), this limitation may be due to the lack of any convention for combining error terms from flux estimates (standard deviation or standard error) with the errors in the classification accuracy of the remotely sensed image. Of the published methods for combining these two types of error term, Dinsmore *et al.* (2009a) tested the sensitivity of their landscape flux estimate to inaccuracies in classification by sequentially altering the proportional coverage of classes by plus or minus 10%. It is not clear how this value of 10% classification error was derived, but the results of this analysis show that, depending on which landscape class is adjusted, the landscape estimate alters by between 3% and 36% for CH_4 flux and by between 1% and 38% for estimated N_2O flux. These authors suggested how their estimate might respond to classification errors, but provided little information on the validity of the chosen error boundaries.

Whilst landscape-scale extrapolations of CH_4 flux rarely include error terms, some more recent studies have (i) measured at a landscape scale so do not require an up-scaling of error term (for example, see Zona *et al.* 2009; Hill *et al.* 2011); (ii) made 'top-down' estimations using inversion methods and derived error terms for landscape estimates, in part, from *a priori* emissions estimates (for example, see Zhao *et al.* 2009); (iii) determined uncertainty though bootstrapping approaches (for example, see Hatala *et al.* 2012); or (iv) spatially weighted extrapolations of error derived replicated chamber measurements (for example, see Teh *et al.* 2011).

The error estimation method used in the current study followed another established method for spatial extrapolation which, unlike the method used by Teh *et al.* (2011), included a quantitative estimate of pixel classification error (Bubier *et al.* 2005). Briefly, the method consists of three stages: (1) calculation of the classification inaccuracy of the remotely sensed image (% of pixels incorrectly classified); (2) calculation of the maximum upper effect of misclassification on fluxes, specifically, increasing the percentage coverage of the strongest emitting class by the percentage of classification inaccuracy calculated in Stage (2) and calculating the resulting change (% increase from original) in landscape estimate; (3) additive combination of the maximum proportional change calculated in Stage (2) with the standard deviation (as % of the mean) of the flux measurements. With two exceptions, the current study followed the above methodology. Firstly, the maximum upper <u>and</u> lower effects of misclassification were calculated to show the range of extreme cases and not just one which increased net landscape emissions. Secondly, the final stage (Stage 3) was discarded due to the lack of support which Bubier *et al.* (2005) provided for the additive combination of error which is considered inappropriate (Field and Miles, 2010). Even without the additive combination of errors used by Bubier *et al.* (2005) a landscape estimate and error term was still calculated in the current study which included (i) the inherent spatial variation of fluxes and gas flux measurement and calculation error; (ii) spatial extrapolation errors. Both these errors revealed that, as the most extreme estimates of CH_4 and CO_2 fluxes as a result of spatial extrapolation errors fell within the one standard error of the mean (as per Table 2.1), further resources would be best directed in reducing the spatial variation in fluxes and errors from gas flux measurements (by increasing the number of sites or increasing number of flux time points) rather than in improving the vegetation classification. The calculation of a landscape estimate with an error term is also useful for subsequent meta-analyses; for example, the IPCC estimate of global CH_4 emissions from 'Natural Sources' (which includes wetlands) included standard deviation of the means of best estimates (FAQ 7.1, Fig. 1 in Denman *et al.* 2007) from several studies (Table 7.6 in Denman *et al.* 2007). Bottom-up estimates from spatially-extrapolated measurements which included error terms would have enabled a meta-analysis of data with appropriate weighting according to variance, but, like other meta-analyses of CH_4 flux data (e.g. Polson *et al.* 2011), the absence of an error term (such as in Wuebbles and Hayhoe, 2002) meant IPCC estimates were not able to distinguish between estimates with varying levels of uncertainty.

2.4.6 Data handling

Not all studies are transparent about how decisions are made regarding flux calculation from observed relationships between headspace concentration and time. For example, Saarnio *et al.* (1997) state that 'clearly disturbed' relationships were removed from the analysis but do not provide further explanation. Specifically, the use of more than two time points enables the identification of single erroneous time points (as in Fig. B.3 (b)), the identification of the shape of the relationship between concentration and time, and the identification of series with no discernable relationship whatsoever. The development of a decision algorithm incorporated a large number of steps, in order to satisfactorily replicate subjective decisions as to removal of single points or entire measurements from the analysis, provided a method which was objective, reproducible and transparent.

The use of r^2 values as the sole criteria for accepting or rejecting a measurement can cause bias through rejection of fluxes close to zero, since experimental noise may be relatively high when compared to the increases in headspace concentrations. One published method which aims to avoid this problem is by Forbrich *et al.* (2010) who, in addition to checks on r^2 values, used filter analysis using an empirically-derived acceptable standard deviation of residuals. Whilst this prevents the removal of low fluxes, it also assumes that such fluxes have a genuine relationship between headspace concentration and time. The algorithm used in the current study makes no such assumption when experimental noise is high enough to prevent the identification of a significant relationship, by producing a flux of zero when such a relationship is not evident (see Fig. B.3 (c)).

2.4.7 Summary

CH_4 fluxes from this upland blanket bog site displayed a distinct seasonal pattern with low emission of CH_4 and some net CH_4 oxidation occurring from January until June, when a dramatic increase in CH_4 emission occurred. Higher emissions of CH_4 fluxes continued throughout a late-autumn shoulder of activity and, in some cases, continued until November and December. The site was a net source of CH_4 and the best landscape estimate of CH_4 flux (± standard error of the mean) was 9.8 (±3.8) g CH_4 m^{-2} $year^{-1}$. Whilst this estimate includes error associated with measurement, the additional consideration of errors associated with the extrapolation of measurements to a landscape-scale estimate resulted in estimates that ranged from 8.6 (±3.7) to 11.1 (±3.8) g CH_4 m^{-2} $year^{-1}$. Differences in the mean estimate of CH_4 flux from areas dominated by different vegetation were observed, but not significant during this study.

Chapter 3 Association of environmental variables with CH_4 flux from upland blanket bog

3.1 Introduction

CH_4 is an important greenhouse gas (Forster *et al.* 2007) produced and oxidised by a number of well described processes (see Wuebbles and Hayhoe, 2002 for one estimate of the global CH_4 budget). It is estimated that net emissions from wetlands account for between 69% and 89% of natural sources of CH_4 emissions (Denman *et al.* 2007), whilst oxidation of CH_4 in dry soils is the only known non-atmospheric process of CH_4 oxidiation (Wuebbles and Hayhoe, 2002). The production and oxidation of CH_4 is undertaken by microbial populations in soils (Le Mer and Roger, 2001), yet the exchange of CH_4 between soil and atmosphere is also affected by above ground vegetation (for example, see Greenup *et al.* 2000; or Strom *et al.* 2003) so in order to incorporate all of these factors which influence CH_4 exchange between soil and atmosphere, measurements must include the soil-plant-atmosphere continuum.

The highest rates of CH_4 production are frequently observed in wetland habitats (for example, see Saarnio *et al.* 1997) and the highest rates of consumption are associated with dry forest soils (for example, see Castro *et al.* 1995). In addition to spatial heterogeneity, variations in CH_4 fluxes also appear to be seasonally dependent with larger fluxes occurring during summer and autumn periods. This has been observed at the current study site (see Chapter 2) and elsewhere in the UK. For example, Hughes *et al.* (1999) measured CH_4 fluxes at fortnightly intervals over a six year period and repeatedly observed higher CH_4 emissions during the summer and autumn than in the winter or spring. The identification of factors which control CH_4 fluxes will lead to better understanding of the dominant systems involved in CH_4 cycling, improve predictions of CH_4 fluxes at locations and during time periods which have not been directly measured, and will improve predictions of the impact that climate change may have on future CH_4 fluxes. To identify significant controls of CH_4 flux at a blanket bog site near Lake Vyrnwy in North Wales (see Fig. 2.1), a regression analysis between fluxes measured monthly over a 14 month period and environmental variables measured continuously over a similar time period was undertaken.

Two approaches are common when identifying environmental controls on the natural variation of CH_4 flux: (i) laboratory based manipulations of environmental conditions of extracted soils or mesocosms (for example, see Moore and Dalva, 1993), and (ii) *in situ* measurements across a range of environmental conditions (for example, see Moore *et al.* 2011). *In situ* manipulations of environmental conditions in field sites are less common, possibly due to the significant resources required to alter conditions in remote locations, but combines features of both common approaches (for example, see Beier *et al.* 2004). Depending on which method is used, statistical analyses are required to identify if there is a significant response of CH_4 flux to the manipulated variable, or whether CH_4 fluxes are significantly associated with a measured environmental variable. A wide range of studies have been undertaken in a variety of habitats and conditions and results are not consistent, even when studies have been made under similar conditions. For example, Bubier *et al.* (1995) showed that CH_4 fluxes observed at a site in a peatland complex in the Northern Study Area of the Boreal Ecosystem-Atmosphere Study in Manitoba (Canada) increased as depth to the water table reduced, whereas Bellisario *et al.* (1999) who sampled in the same study area show the inverse relationship. No hypothesis was presented to explain how these conflicting results were found from measurements at the same habitat, but they were not a result of inconsistencies with the method of water table measurement. The value of depth to water table, which is used in the current study, increases as the water table moves further below the soil surface, being a negative value when the water table is above the surface; however an alternative reporting convention 'water table position' decreases as the water table moves further below from the soil surface and is a positive value when the water table is above the surface.

The direct controls of net CH_4 fluxes can be described as the balance between the microbial production and oxidation of CH_4 in the soil, combined with the rate of exchange of CH_4 between soil and atmosphere (Le Mer and Roger, 2001). Consequently, it is expected that any environmental conditions which directly, or indirectly, influence any of these components will exert control over CH_4 fluxes. For example, temperature has been shown to control CH_4 fluxes as it directly influences the rate of CH_4 production and other processes which are involved in CH_4 production, such as acetate production (Segers, 1998). Alternatively, a higher level of radiation has also been shown to control CH_4 fluxes as it leads to higher substrate provision though increased plant growth. Subsequently, a large number of environmental conditions have been shown to be significant controllers of CH_4 fluxes.

Published examples include general meteorological conditions such as air temperature (Ward *et al.* 2007), shortwave incoming radiation (Hendriks *et al.* 2010), photosynthetically active radiation (PAR; Ward *et al.* 2007), humidity (Tsuyuzaki *et al.* 2001) rainfall (Kettunen *et al.* 1996) and atmospheric pressure (Tokida *et al.* 2007); soil conditions such as soil temperature (Becker *et al.* 2008), water table (Bubier *et al.* 2005), soil moisture (Dinsmore *et al.* 2009a), pH, soil conductivity (Bubier *et al.* 1995) and redox potential of the soil (Conrad, 1996); soil concentration of CH_4 (Dinsmore *et al.* 2009a), Ca^{2+} (Bubier *et al.* 1995), N and SO_4^{2-} (Silvola *et al.* 2003); and biological components of systems such as vegetation cover (Bubier *et al.* 1995), esterase activity (Freeman *et al.* 1998) and transcriptional dynamics of genes associated with methanogenesis (Freitag *et al.* 2010). The variety of results from previous studies makes the analysis of environmental controls of CH_4 fluxes at any site both interesting and unpredictable, but the most commonly identified environmental controls over CH_4 fluxes are water table depth and soil temperature. Not only are these variables most commonly found as significant controls of CH_4 flux in a variety of studies, they are also predicted by existing theoretical models of CH_4 flux. Models based on the vertical distinction of the acrotelm and catotelm within the soil profile (Clymo and Pearce, 1995; Le Mer and Roger, 2001) suggest water table is a key driver of net CH_4 flux as the size of the aerobic proportion of the soil profile can influence rates of methanogenesis, methanotrophy and CH_4 exchange between soil and atmosphere. Temperature is also considered a key driver of fluxes as it influences all biological activity including rates of CH_4 production (for example, see Segers, 1998), CH_4 oxidation (for example, see Crill *et al.* 1994) and substrate provision for methanogens (for example, see Eriksson *et al.* 2010).

Studies typically use concurrent measurements of environmental conditions to identify controls on CH_4 fluxes. Even when seasonal measurements of environmental conditions are used as independent variables in models of CH_4 fluxes, it is typically difficult to predict a mean seasonal flux (for example, see Bubier *et al.* 2005). However, observations of hysteresis effects of CH_4 fluxes due to changes in water table (Moore and Roulet, 1993), temperature (Updegraff *et al.* 1998) and PAR (Joabsson *et al.* 1999) suggest that environmental conditions prior to the day of flux measurement may provide better predictions of CH_4 flux. Previous studies have used a variety of techniques in examining prior conditions which range from quantitative cross correlations (Kettunen *et al.* 1996) to visual identification of hysteresis effects (Song *et al.* 2003). A limitation of the current study is the seasonal covariance between several environmental variables. These include a temperate seasonal pattern of temperature, radiation and, to some extent, humidity. Such multicollinearity may make it hard to identify the importance of individual environmental controls (Field and Miles, 2010). A satisfactory solution is the complimentary manipulation of environmental conditions of extracted soils in otherwise controlled environments which has been undertaken with water table using samples from the same field site (Lukac *et al.* personal communication).

It is possible to combine approaches of experimental manipulation and *in situ* measurement to produce landscape scale manipulations but requires a large amount of resources to undertake any such manipulation. Fortuitously, the current managers of the Lake Vyrnwy site, the Royal Society for the Protection of Birds (RSPB), had obtained extensive funding for the blocking of drains from the European Union LIFE project. The management of the blanket bog around Lake Vyrnwy has varied historically, but has often focused on the delivery of a single ecosystem service (*sensu* Millennium Ecosystem Assessment, 2005) including recreational hunting, water provision, the grazing of livestock, or biodiversity conservation (Roberts, 2000; Bowker *et al.* 2007). One practice applied to large areas of the blanket bog during the 1960's and 1970's, was the creation of drains to dry the site and improve conditions for livestock (Wilson *et al.* 2010). A subsequent, contrasting approach, which has also been implemented at many other blanket bog sites in the UK (Armstrong *et al.* 2009), has been the blocking of previously man-made drains in order to restore hydrological conditions and improve the condition of the blanket bog for several rare bird species (Wilson *et al.* 2010). This also provided a platform for studying the effect of manipulating one particular environmental factor: hydrological conditions.

Observations of a spatial association between high CH_4 fluxes and wetter sites (Bubier *et al.* 1993) together with results from laboratory-based manipulative experiments on extracted peatland samples (Moore and Dalva, 1993, *inter alia*) suggest that the blocking of drains will cause an increase in CH_4 fluxes. However, results from *in situ* studies conducted over spatially or temporally larger scales are less clear. For example, Hughes *et al.* (1999) drained a bog which, when compared with a control site, initially led to lower CH_4 fluxes. Continued monitoring of CH_4 fluxes in the Hughes *et al.* study showed that CH_4 fluxes of the drained site had returned to control levels after three years, suggesting the treatment had no long-term effect. Another *in situ* study which failed to clearly identify the effect of treatment was the comparison of a restored peatland site, with blocked drains, and a non-restored site with intact drains (Waddington and Day, 2007). The restored site had significantly higher CH_4 fluxes than the control site in two of the three years following the drain blocking, and CH_4 fluxes at the restored site were higher in all years following the treatment when compared to the year prior to the blocking of drains. Unfortunately, as the restored site had significantly higher CH_4 fluxes than the control site in the year prior to restoration, and as CH_4 fluxes at the control site were also higher in all years following the treatment, it is not clear whether such differences were due to the experimental manipulation, or the inherent spatial and temporal variation in CH_4 fluxes. Regardless of *a priori* expectations, any experimental design should enable the clear identification of any treatment effect.

The studies presented within this chapter were aiming to identify significant *in situ* associations between CH_4 flux and a large number of environmental conditions in an upland blanket bog. These included both conditions observed at the point of flux measurement and conditions prior to the point of measurement. An additional hypothesis which was tested was that CH_4 flux was significantly altered due to a landscape-scale manipulation of hydrological regime.

3.2 Materials and methods

3.2.1 Study site and flux measurements

The 22 km^2 of upland blanket bog around Lake Vyrnwy, North Wales (described in Section 2.2.1) was used as the study site for a regression-based approach to landscape-scale estimates of CH_4 flux and subsequent comparison with other extrapolation methods. The CH_4 flux measurements, made with non-steady state chambers (see Section 2.2.2), were used as dependant values in the construction of the following regression-based models.

CH_4 fluxes were measured monthly between December 2008 and January 2010 from four vegetation types, replicated around three meteorological stations (see Section 2.2.1). Five flux measurements were made at each combination of site and vegetation type and the sampling strategy was designed to incorporate variation from areas dominated by four vegetation types, grass, heather, Juncus and sedge. Fluxes were calculated from five consecutive samples, extracted from the chamber headspace over a total period of between 80 and 120 minutes. The exact time of extraction was recorded and after GC analysis for CH_4 and SF_6, the slope of linear regression between CH_4 concentration and time for each individual measurement was calculated. At the start of each measurement, CH_4 was added to each chamber headspace to enable detection of CH_4 oxidation and SF_6 was also added to observe any leakage from the headspace during the measurement period. Each flux was calculated using an algorithm which was designed to objectively remove any erroneous data time points from a single series and to determine if leakage should be compensated for, or if a measurement should be entirely discarded. See Sections 2.2.2 and 2.2.3 for further details.

An annual landscape estimate, derived from linear interpolation between monthly CH_4 measurements and spatially extrapolated using the proportional coverage of each vegetation type, calculated using IKONOS images of the site was used for comparison purposes. Survey data collected at the site were used to both supervise and validate the vegetation classification, enabling the calculation of proportional coverage of each vegetation type and the accuracy of the classification. See Section 2.2.4 for further details.

3.2.2 Environmental data

A dedicated meteorological station (WS-GP1 and all associated sensors, listed below, all from Delta-T Devices, Cambridge, UK) was established at each of three sampling sites described in Section 2.2.1 during 2008 (see Fig. 2.1) and was positioned within 10 m of each vegetation area where flux measurements were to be made. The following environmental variables were recorded at each site from May 2008 to January 2010: air temperature and relative humidity (RH) from a combined sensor (RHT2nl-CA) positioned 2 m above ground, photosynthetically active radiation (PAR, 400 – 700 nm; QS2), solar radiation (300 – 3000 nm; D-PYRPA-CA), wind speed and wind direction (D-034B-CA) and rainfall (RG2+WS-CA). In addition, soil temperature (sensor type ST1, installed 10 cm below the surface) and depth to water table (water table, measured using 30 mm wide piezometers inserted up to a depth of 1 m) were measured at each of the four vegetation types around each meteorological station. All variables were measured automatically, with the exception of water table which was measured manually when gas flux measurements were made. Hourly mean values were calculated for soil temperature, air temperature, PAR, solar radiation, humidity and wind speed. Rainfall was summed to produce hourly totals, and hourly values (measured on-the-hour only) were also recorded for wind direction.

Missing hourly values for the automatic sensors, due to equipment failure, livestock damage, etc., were gap-filled with estimates calculated from one of two methods, depending on the length of gap. For data gaps of a single hour, an estimate was calculated from the mean of the adjoining values, but for data gaps of more than one hour estimates were made using regressions between the sensor with the missing values (dependant variable) and sensors which were fully functioning during the data gap (independant variables). Regression models used to estimate values for each data gap were constructed subject to two main criteria. (i) At least one independent variable, produced from a similar sensor type at another location or vegetation type (soil and air temperatures were considered similar, as were PAR and solar radiation), had to be present for the entire data gap. If there was more than one non-missing variable present for the entire gap, a multiple regression approach was used. (ii) The coefficient of determination (r^2) for the correlation between actual and predicted values had to be greater than 0.8. If no similar non-missing variable was present during a data gap, multiple models were constructed across shorter time periods which, once estimated values were combined, filled the entire data gap. When a multiple regression approach was required, a forward-selection technique was used that also included an additional step to remove previously-added independent variables which were no longer significant ($p<0.05$, PROC REG procedure with the SELECTION=STEPWISE option on SAS®, v9.2). An example of the resulting models for data gaps in the soil temperature record, and the strong correlation between predicted and actual values, are shown in Fig. 3.1. In reality, the data gaps were only several hours or days and simple regression models frequently yielded r^2 values greater than 0.95 resulting in high confidence in the quality of gap filled data. Further details of each data gap-filling regression model are included in Appendix C.

3.2.3 Regression between CH_4 flux and environmental variables

The environmental variables (independent values: soil temperature, air temperature, PAR, solar radiation, humidity, wind speed, rainfall and water table) which best explained the variations seen in CH_4 flux measurements (dependent values) for each vegetation type were identified using regression approaches.

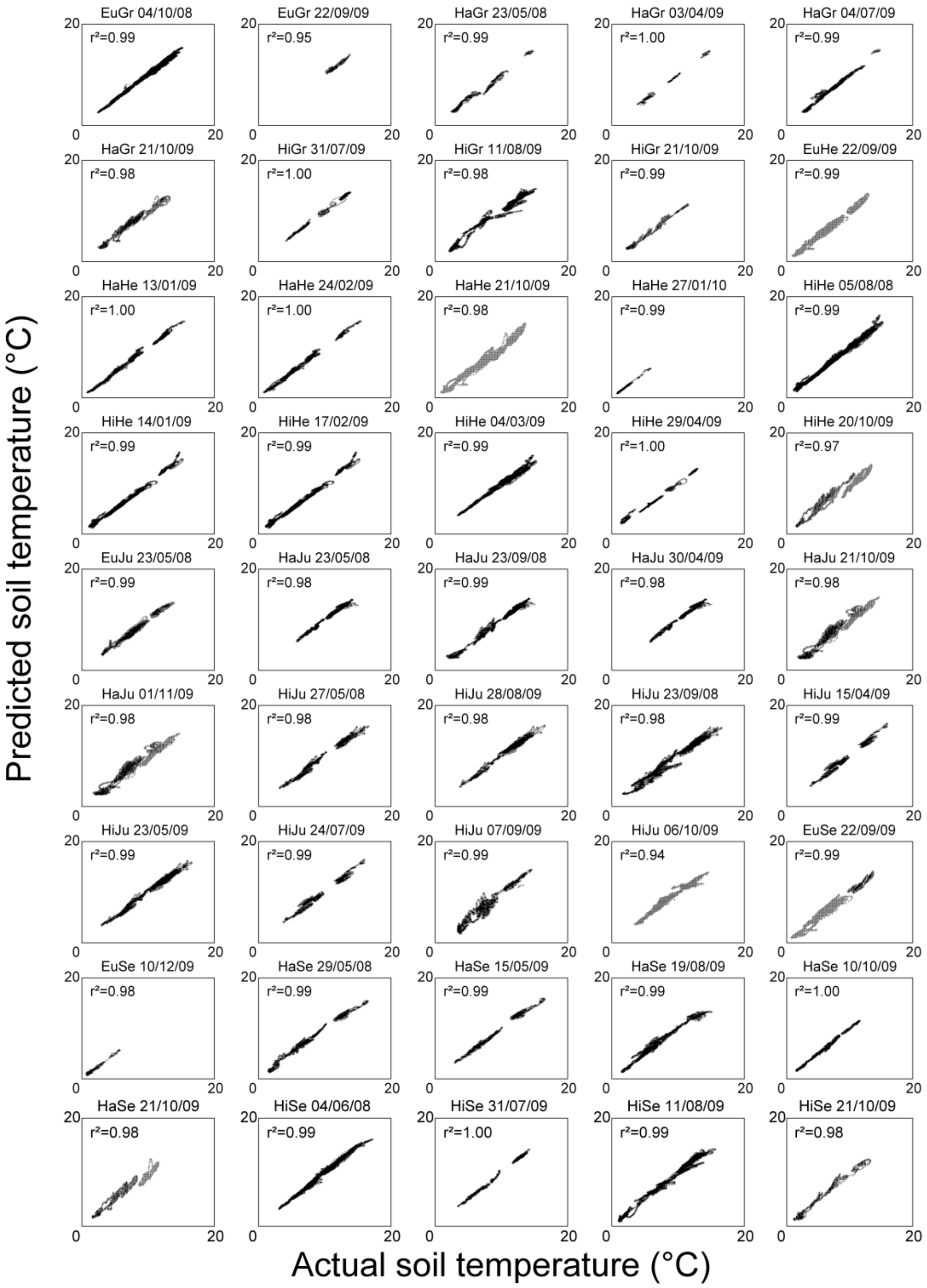

Fig. 3.1 The results from data gap-filling models for each period of missing soil temperature data showing strong correlation values between predicted and actual values. Each model is labelled with a four letter code, where the first two characters define location (Eu = Eunant, Ha = Hafod and Hi = Hirddu) and the last two characters define type of vegetation (Gr = grass, He = heather, Ju = Juncus and Se = sedge), and the starting date of the data gap.

3.2.3.1 *Multiple regression between CH_4 flux and concurrent environmental variables*

Following a frequently used approach (see, for example, Granberg *et al.* 1997; Moore *et al.* 2011; Worrall *et al.* 2007b; Dinsmore *et al.* 2009b) multiple regressions between CH_4 fluxes and all their associated environmental variables were made. All of the CH_4 flux measurements were analysed together in a single model, and subsets of the CH_4 flux measurements, subsetted according to vegetation type, were also analysed in separate multiple regression models for grass, heather, Juncus and sedge. The environmental measurements used as independent variables, and referred to as concurrent measurements, were those taken at the hour closest to the first extraction from the chamber headspace, with the exception of wind speed, rainfall and water table which used daily measurements of wind run (the product of an instantaneous wind speed measurement and period of time), daily total rainfall, and water table measured in conjunction with all flux measurements. A forward step-wise multiple regression approach was used that included an additional step to remove any independent variables which, having been significant ($p<0.05$) during an earlier step, became non-significant as other independent variables were added in subsequent steps (SAS® v9.2). The use of daily values of wind speed and rainfall as independent variables was required as daily values had been used to construct data gap filling regression models (see Appendix C). The positive skew of the distribution of the CH_4 flux measurement, indicated by the difference between the mean (1.01 mg CH_4 m^{-2} h^{-1}) and median (0.03 mg CH_4 m^{-2} h^{-1}) CH_4 flux measurement, suggested that flux measurements required transforming to achieving a more normal distribution. Subsequently, CH_4 flux measurements were converted to $\log_{10}$ (mg CH_4 m^{-2} d^{-1} + 2.7) to correct for the positive skew and used as the dependent variable in regression models. The results of these models were compared with results from models which used untransformed fluxes as dependent variables.

3.2.3.2 *Single regression between CH_4 flux and the running averages of environmental variables*

The late-autumn shoulder of activity seen in the seasonal pattern of CH_4 fluxes (see Fig. 2.2 and the discussion in Section 2.4.2) and other observations of delayed response of net CH_4 exchange to environmental conditions (Hughes *et al.* 1999; Lukac et al. personal communication; Fenner *et al.* 2005) suggested an alternative approach to the regression between CH_4 fluxes and environmental variables could also be taken. This approach used the average of environmental measurements from the period prior to the day of flux measurement, referred to as the running average. The running average was calculated as the moving average of *n* daily values, where *n* ranged from 0 (the day of the flux measurement) to 180 (the period ranging from the day of flux measurement to 180 days prior to flux measurement). Daily values were defined as daily mean measurements for soil temperature, air temperature and humidity, and as daily total measurements for PAR, solar radiation, wind speed (also defined as daily total wind run: the distance covered in a day) and rainfall. Regressions were made using all CH_4 flux measurements, and using four subsets of measurements (grass, heather, Juncus and sedge) with each environmental variable being used as a single independent variable in a series (0 to 180 days) of separate single regression models (SAS® v9.2, PROC REG with no additional options).

In order that the running average could be calculated for depth to water measurements, and in the absence of automated measurements throughout the study period, daily water table measurements were modelled. A crude hydrological model using rainfall as the single independent variable was constructed for each combination of site and vegetation type. An association between water table measurements in peatlands and rainfall measurements on the day, or the days prior to water table measurement (Evans *et al.* 1999; Weiss *et al.* 2006) has been demonstrated, so the running average over 30 days (as described above) was used to identify what period of rainfall best explained the observed variation in water table. Individual models were created for each combination of site and vegetation type and the period of rainfall which best described water table varied from 0 (the day of water table measurement) to 12 (the average of 12 days prior to water table measurement), as did r^2 values for each model: 0.169 to 0.878. The running average of rainfall which produced the model with the highest r^2 for each site and vegetation type was selected to model water tables at the relevant site. Two of these models (Juncus at Hafod and at Hirddu) were not significant but, in the absence of other daily values of water table, were still used.

3.2.3.3 Multiple regression of CH_4 flux and the running averages of environmental variables

A fully inclusive multiple regression analysis of all possible combinations of eight running averages, each over 0 to 180 days, was not considered practical as it would have resulted in the running of ca. 1 x 10^{18} multiple regression models. Instead, soil temperature, solar radiation and modelled water table were selected as the only independent variables for the multiple regressions of running averages with CH_4 flux. Whilst air temperature and PAR were also considered to be likely significant regressors of CH_4 flux, they were excluded due to their co-variation with soil temperature and solar radiation, respectively.

Running averages over different periods from the same sensor were not used together as independent variables in the same model, but ca. 5 x 10^6 multiple regression models for each vegetation type were still produced. Attention is drawn to the increased probability of Type I errors due to the high number of individual models constructed (Field and Miles, 2010). Consequently, the interpretation of the results was limited when viewing each single regression model and, when viewing this analysis in its entirety, only consistent patterns of association between variables and fluxes were considered as significant (see Section 3.4).

3.2.4 Impact of ditch blocking on CH_4 flux

3.2.4.1 Study site description and experimental design

Measurements were made in the upland blanket bog around Lake Vyrnwy, North Wales (as generally described in Section 2.2.1) and focused within three distinct catchments (see Fig. 3.2): Eunant Fach (centred around SH 92651 22937), Eunant Fawr (SH 94164 22248), and Eiddew (SH 93411 24807). One of the dominant features of the blanket bog at the Lake Vyrnwy site were the large number of man-made ditches (also known as grips) which were cut across the hillside in the 1950-1970's to increase drainage in favour of sheep grazing (Wilson *et al.* 2011a). Whilst this management technique was used at many other blanket bogs across the UK (Worrall *et al.* 2007a), the management of the blanket bog at Lake Vyrnwy was changed to reverse any artificial drainage and 100 km of drains have been blocked since 2007 to improve the unfavourable status of the site (Wilson *et al.* 2011a). In the Eunant Fach, Eunant Fawr and Eiddew catchments the blocking of drains was not uniformly implemented, but a fully-replicated block design was established so that within each of the three catchments used in this study, a pair of sub-catchments was created with each sub-catchment either being assigned the drain blocking treatment or retained as an unblocked control (see Fig. 4.2). All sub-catchments were selected to be a similar size (mean (±SEM) size was 30.5 (±3.3) ha), and each pair was positioned on the same hillside, no more than 250 m apart, so a similar aspect and slope was maintained. The decision of which sub-catchment received the blocking treatment within any particular pair was made at random so this fully-balanced design could be used as a basis for studying the effect of drain blocking on CH_4 fluxes.

3.2.4.2 Flux measurements and data handling

Several sets of measurements were made within each sub-catchment to identify any differences in CH_4 fluxes in a variety of micro-sites. Specifically, 10 flux measurements were

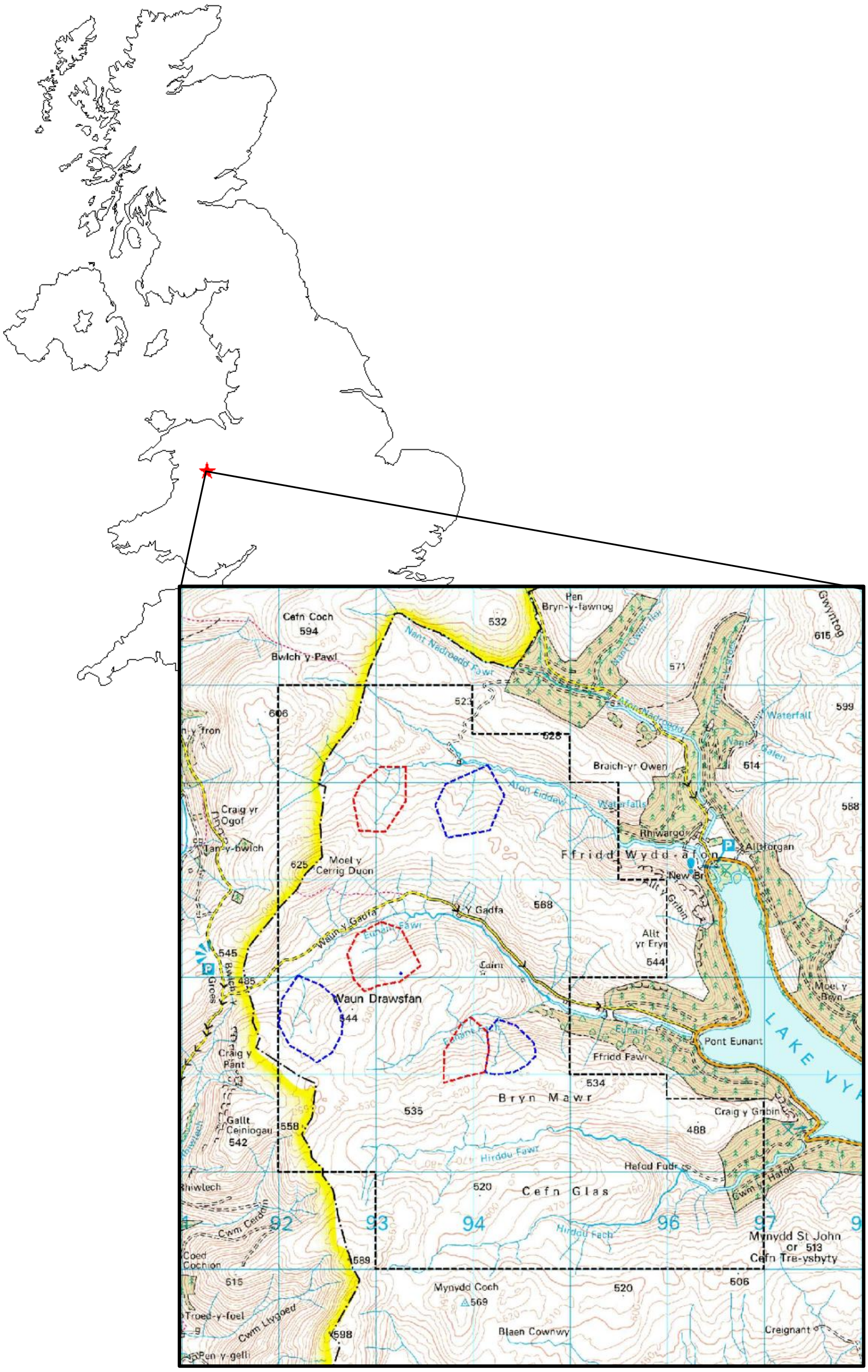

Fig. 3.2 Location of Lake Vyrnwy with the study site for the impact of ditch blocking on CH_4 flux. The three pairs of blocked (red dashed line) and unblocked (blue dashed line) sub-catchments are marked.

made at all combinations of two vegetation types, heather and sedge, two elevations, lower (470-475 m.a.s.l.) and upper (520 - 525 m.a.s.l.) and two management techniques, blocked and unblocked. Specific locations within each combination of factors were arbitrarily selected prior to the start of the campaign to enhance unbiased sampling within each sub-catchment (e.g. with regards distance to drains etc.). Flux measurements were made during a single campaign from the 24th to the 27th March, 2009 with static non-steady state chambers as described in Section 2.2.2 and using SF_6 for leak detection. Briefly, fluxes were calculated from five consecutive samples, extracted from the chamber headspace over a mean (±SEM) total period of 87.8 (±1.07) minutes. The exact time between extractions was recorded and after GC analysis for CH_4 and SF_6, the slope of linear regression between CH_4 concentration and time for each individual measurement was calculated. At the start of each measurement, CH_4 was added to each chamber headspace to enable detection of CH_4 oxidation and SF_6 was also added to observe any leakage from the headspace during the measurement period. Each flux was calculated using an algorithm which was designed to (i) objectively remove any erroneous data time points from a single series, (ii) determine if leakage should be compensated for, and (iii) determine if a measurement should be entirely discarded. See Sections 2.2.2 and 2.2.3 for further details.

Seasonal CH_4 flux measurements made during 2009 (see Fig. 2.2) revealed March to be a period of relatively low net CH_4 flux, so a second campaign part was undertaken in August 2010, when measurements were repeated in a limited number of micro-sites in all sub-catchments. Expectations that aerenchymous plants are important pathways for CH_4 emissions in wet locations (Greenup *et al.* 2000) and the observation that hydrological conditions at elevations below blocked drains are strongly effect by drain blocking at Vyrnwy (Wilson *et al.* 2010) meant that comparisons between blocked and unblocked sub-catchments were only made at lower elevation sedge micro-sites. Fluxes were measured within 5 m of the first campaign, but did not use the exact same location.

Two final statistical comparisons were made: the first using all fluxes from the campaign in March 2009 and, after testing all groups for normality and homogeneity of variance, compared all three effects of drain blocking, elevation and vegetation. The second comparison was restricted to data obtained from lower elevation sedge sites during March 2009 and August 2010 and used an appropriate test on the effect of drain blocking and season.

3.3 Results

3.3.1 Environmental variables

3.3.1.1 Water table

Time plots of all environmental variables measured throughout the study period, from each site and each vegetation type, are shown in Fig. 3.3 to Fig. 3.15. There was no clear seasonal pattern for the manual (Fig. 3.3) or modelled (Fig. 3.4 to Fig. 3.6) measurements of water table but the shallowest manual measurements, which occurred during November 2009, coincided with the largest amount of rainfall (Fig. 3.11). As expected, the modelled daily values of water table showed higher variability than monthly manual measurements. In addition, modelled values produced lower minimum values at most sites and vegetation types (Fig. 3.4 to Fig. 3.6). Due to the close proximity of the grass and Juncus vegetation types at the Eunant site, water table measurements for both vegetation types at this site were taken from the same series of piezometers. Water table measurements could not be made at any sites in January 2009 due to frozen conditions.

The assumption of sphericity between monthly manual measurements was not testable due to insufficient degrees of freedom but assuming that sphericity was violated, degrees of freedom were adjusted ($\hat{\varepsilon} = 0.2933$). Results of a repeated measures ANOVA showed a significant effect of vegetation type ($p = 0.012$), a significant within-vegetation effect of sampling month on water table ($p < 0.001$) but no interaction between vegetation type and time of sampling ($p = 0.653$). *Post hoc* testing within each month showed significant effects ($p < 0.00385$) of vegetation type on water table during December 2008 (between grass and sedge), April 2009 (between grass and heather, and between grass and sedge), June 2009 (between grass and heather, and between grass and sedge) and November 2009 (between grass and sedge) as illustrated in Fig. 3.3.

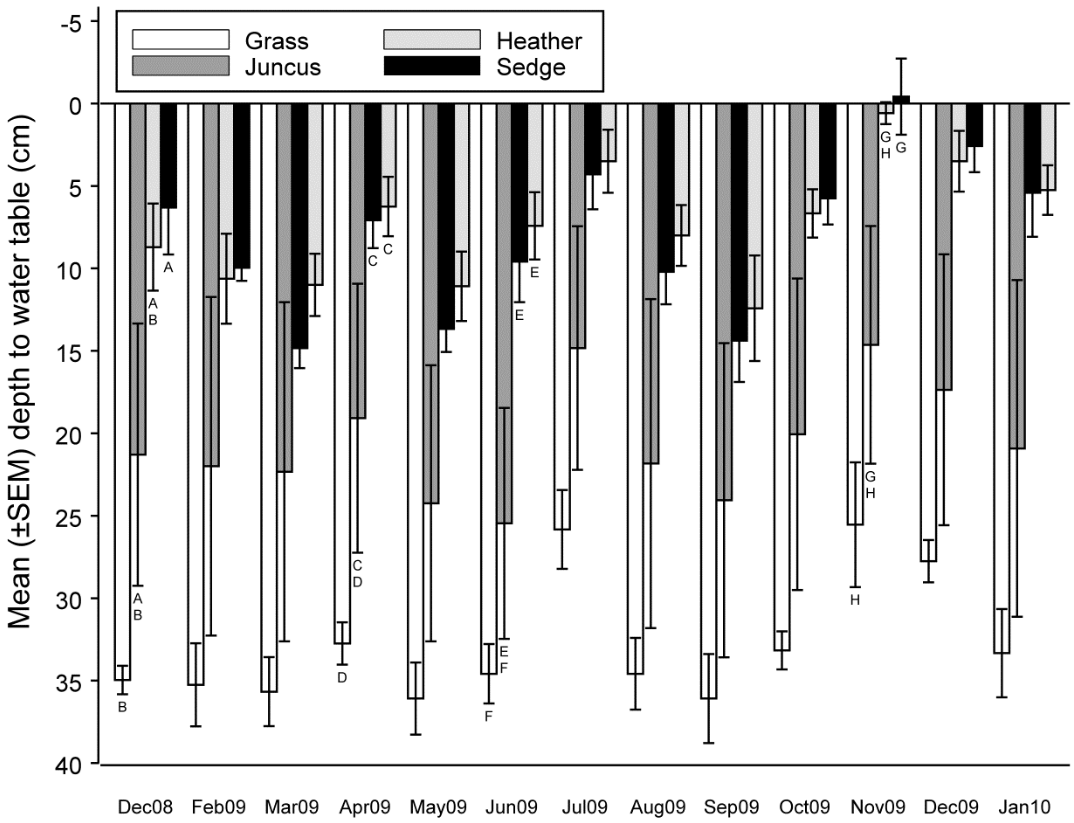

Fig. 3.3 Mean (±SEM) depth to water table (cm) for four vegetation types, made at the same time as with each flux measurement from December 2008 to January 2010, n = 3. No measurements were possible in January 2009 due to frozen conditions. Within each sampling month, vegetation types with the same letters are not significantly different from each other (*post hoc* Duncan's test with a Bonferroni correction at the p = 0.00385 level).

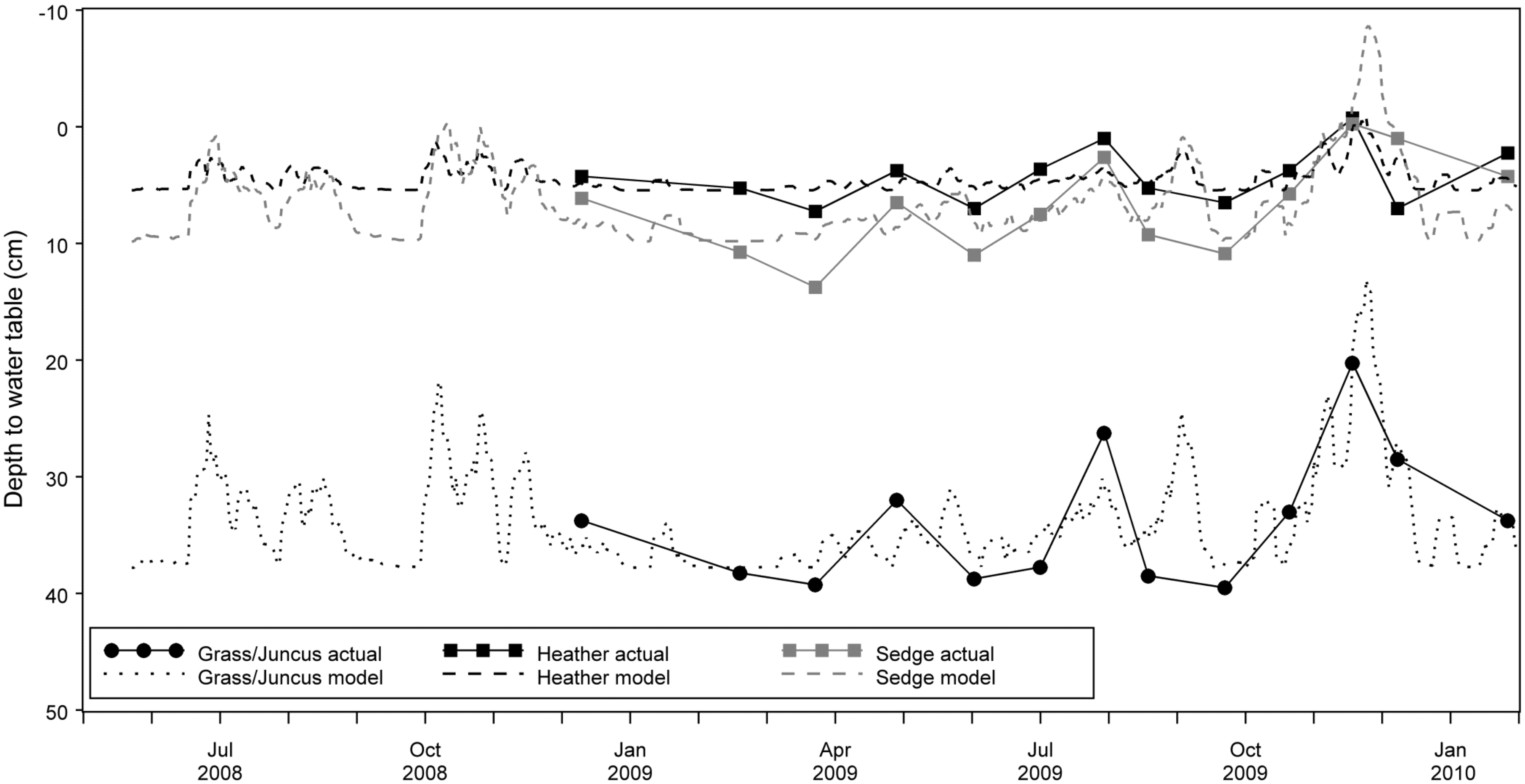

Fig. 3.4 Modelled and measured depth to water table (cm) from three vegetation types at the Eunant site from May 2008 to January 2010. The same actual measurements were used for both grass and Juncus vegetation types at this site. No measurements were possible in January 2009 due to frozen conditions.

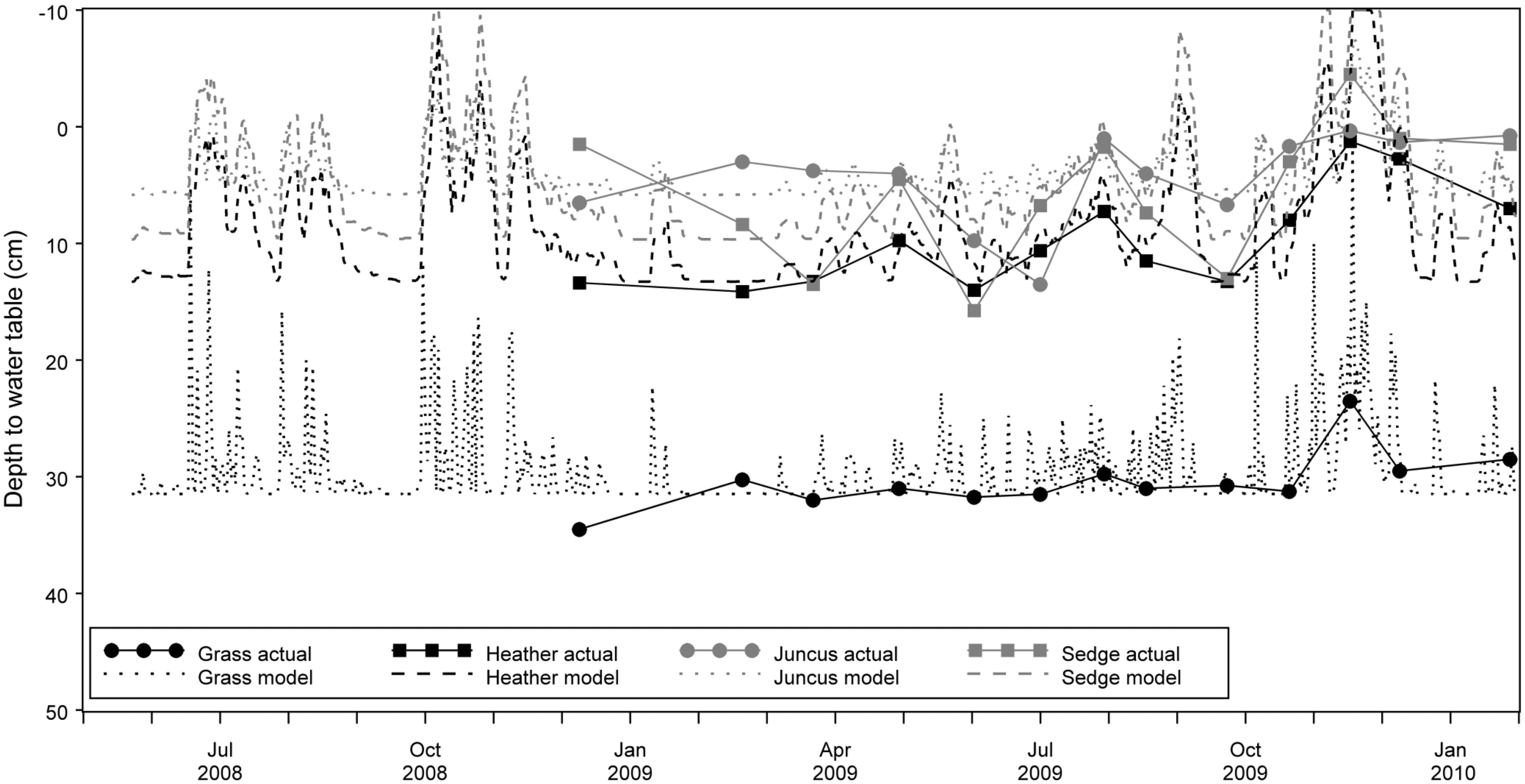

Fig. 3.5 Modelled and measured depth to water table (cm) from four vegetation types at the Hafod site from May 2008 to January 2010. No measurements were possible in January 2009 due to frozen conditions.

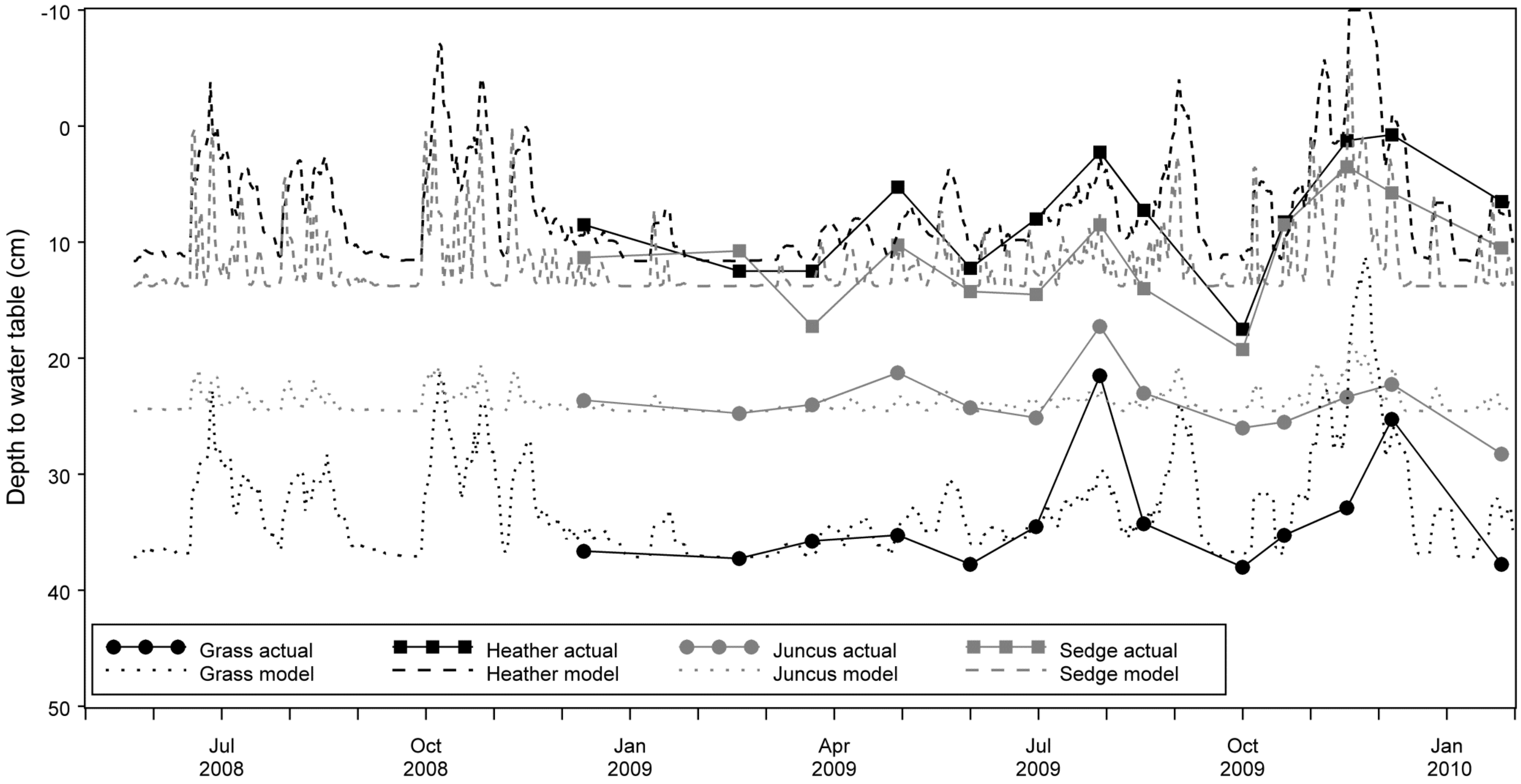

Fig. 3.6 Modelled and measured depth to water table (cm) from four vegetation types at the Hirddu site from May 2008 to January 2010. No measurements were possible in January 2009 due to frozen conditions.

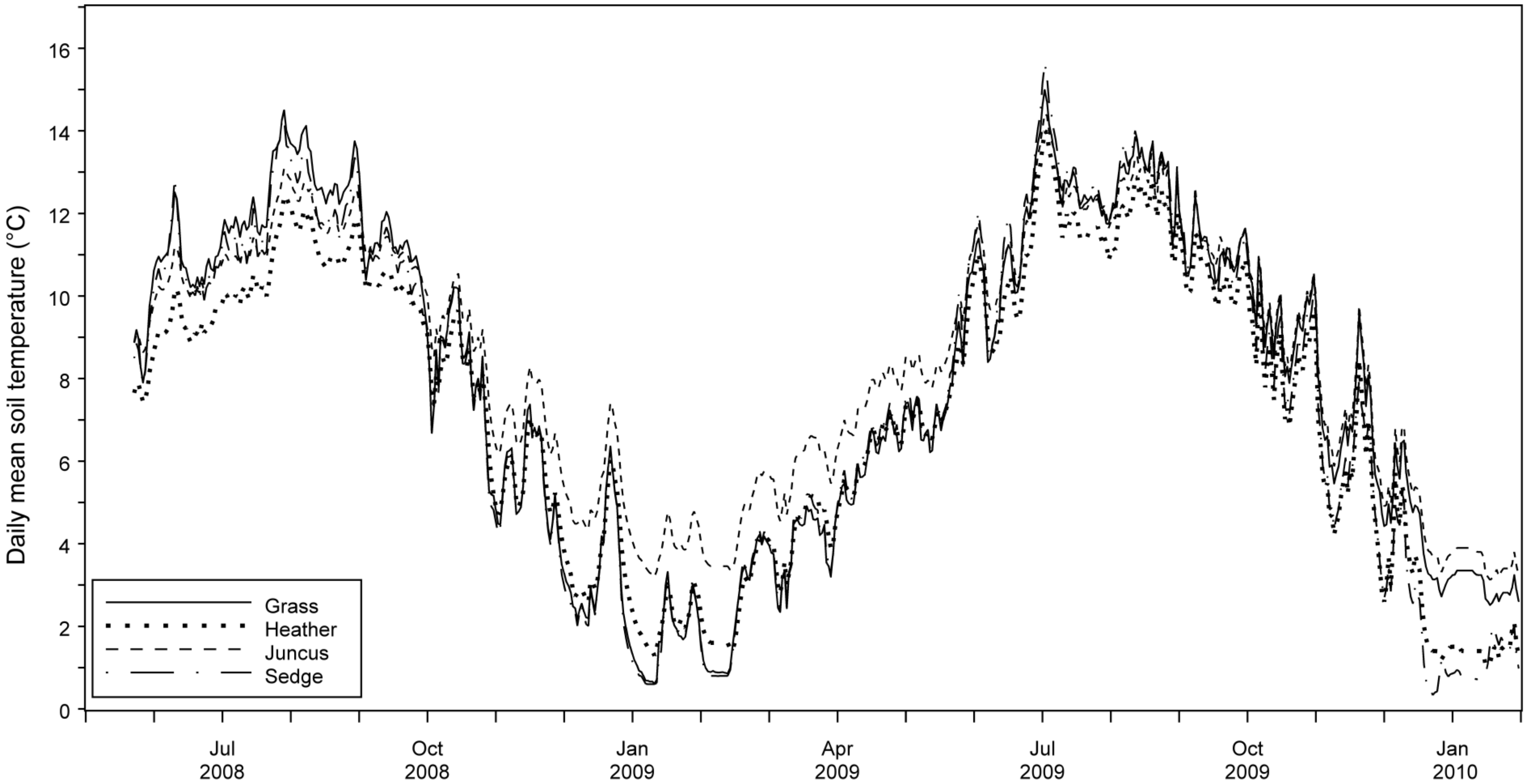

Fig. 3.7 Daily mean soil temperature (°C) measured at a 10 cm depth from four vegetation types at the Eunant site from May 2008 to January 2010.

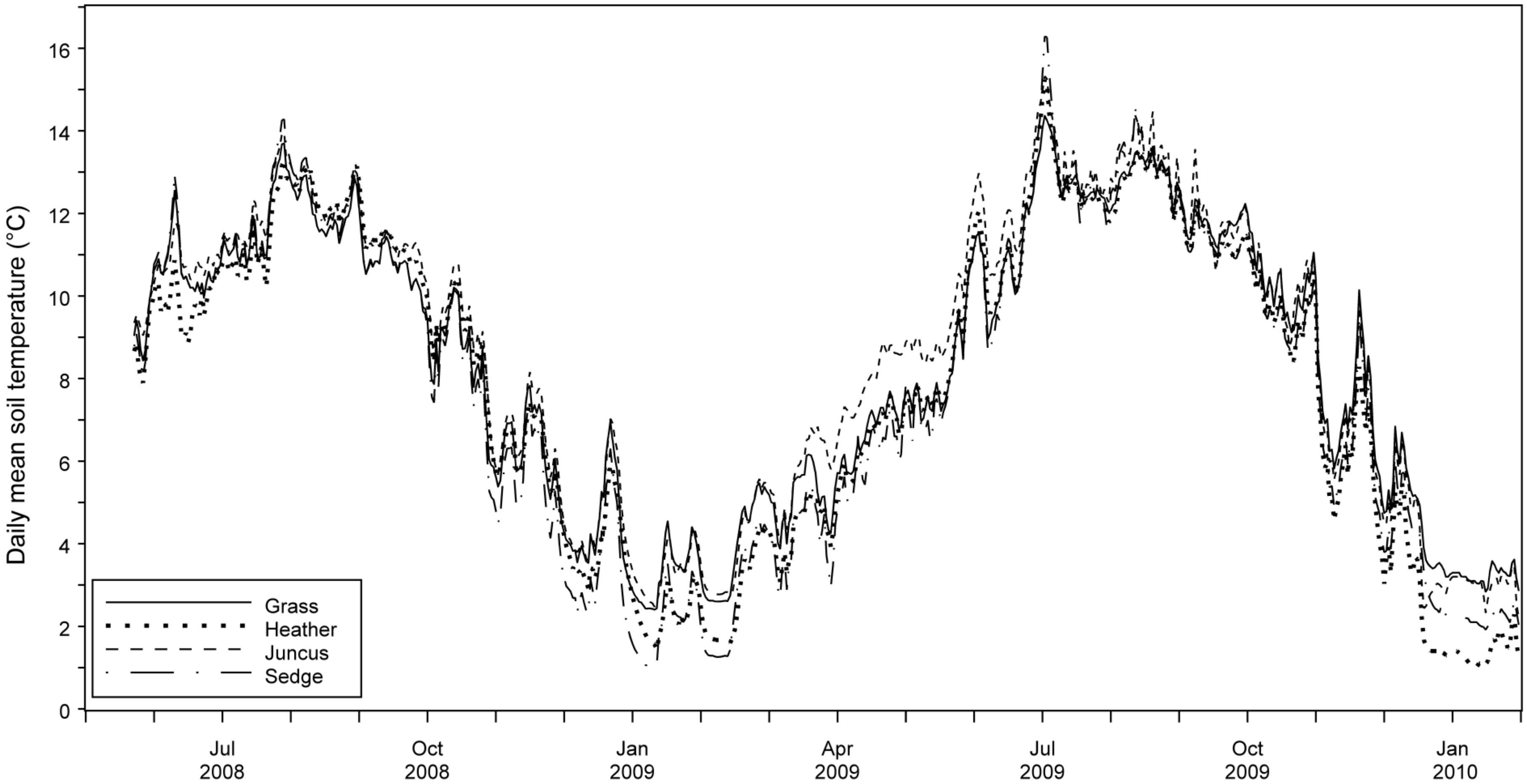

Fig. 3.8 Daily mean soil temperature (°C) measured at a 10 cm depth from four vegetation types at the Hafod site from May 2008 to January 2010.

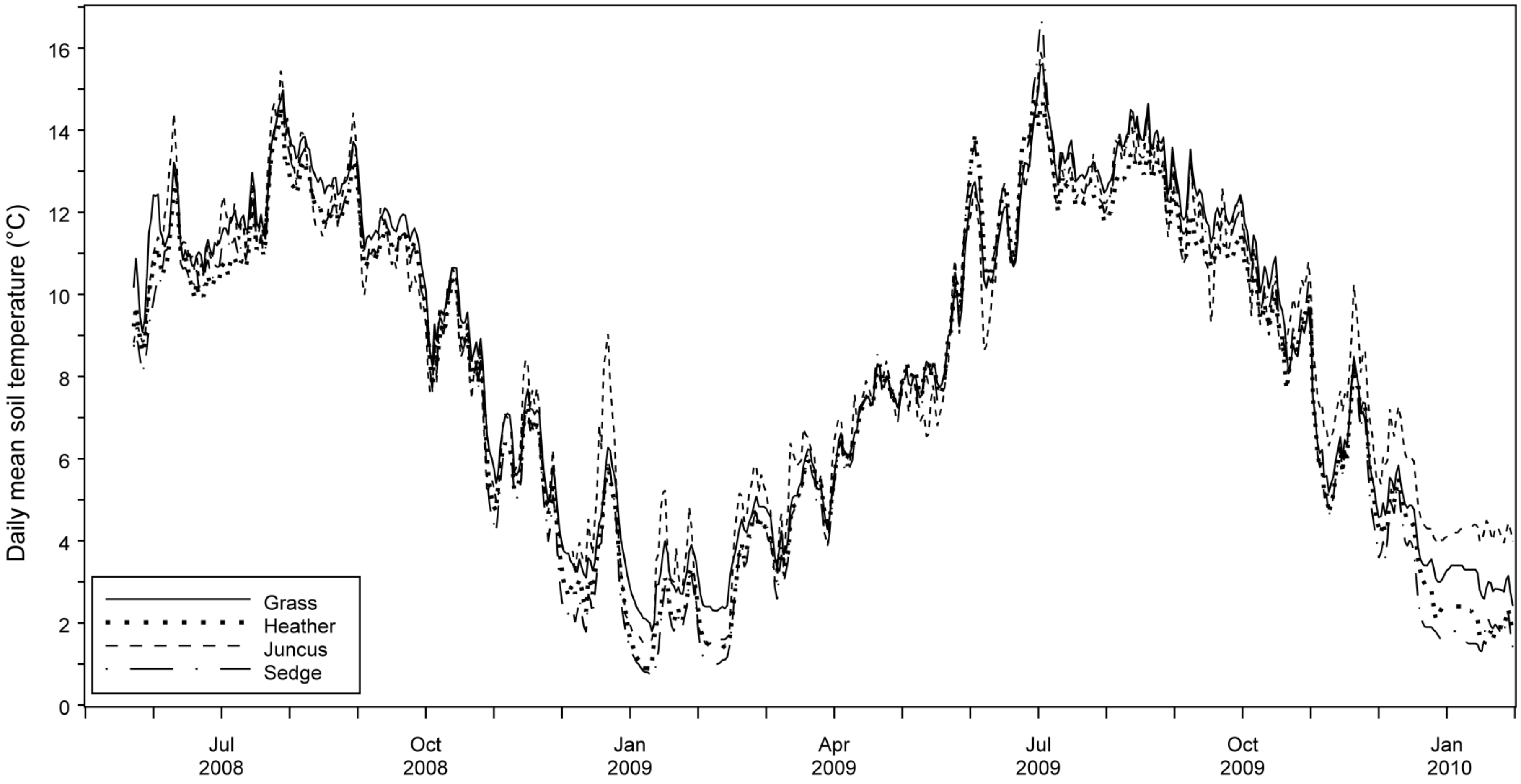

Fig. 3.9 Daily mean soil temperature (°C) measured at a 10 cm depth from four vegetation types at the Hirddu site from May 2008 to January 2010.

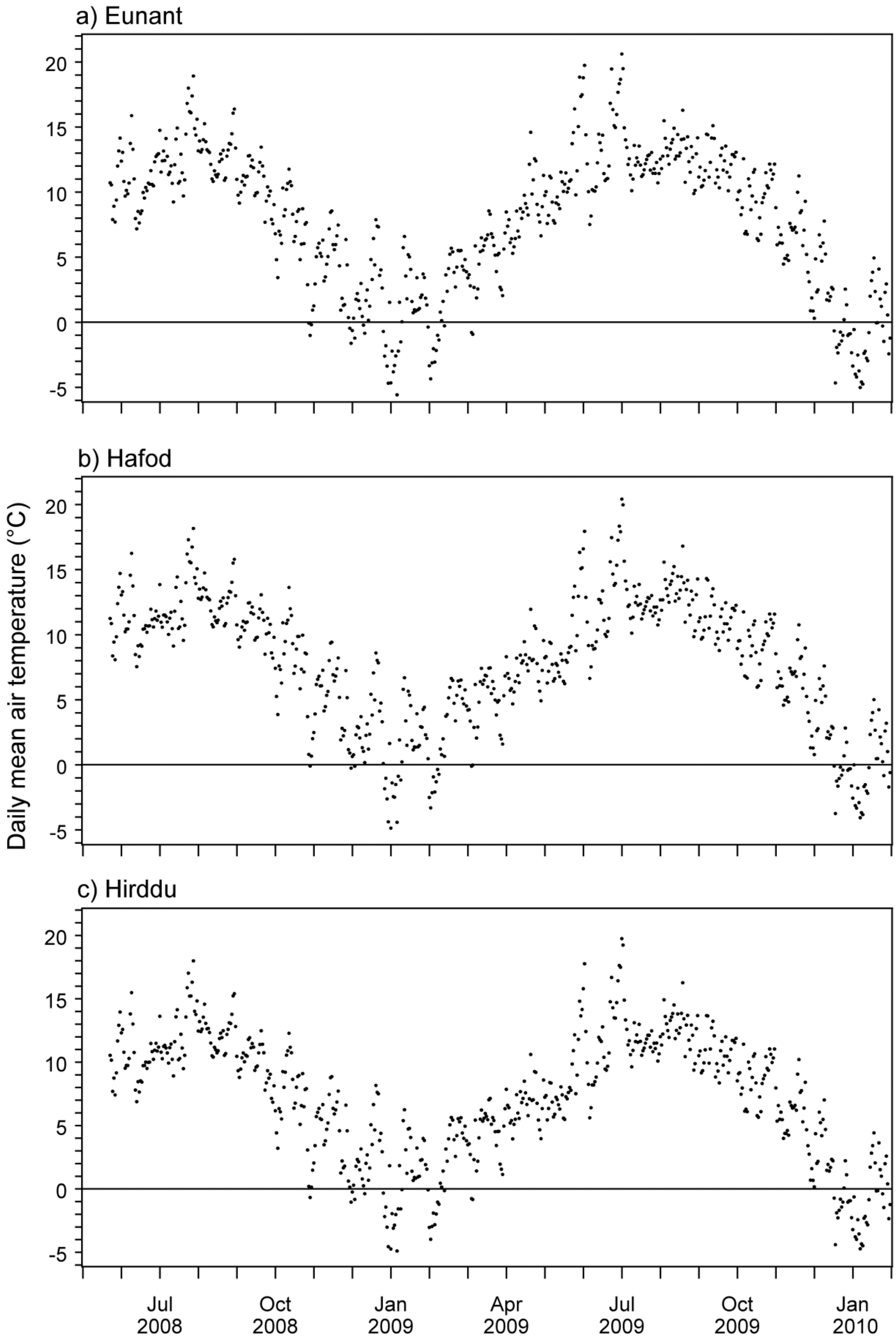

Fig. 3.10 Daily mean air temperature (°C) from the Eunant, Hafod and Hirddu sites during May 2008 to January 2010.

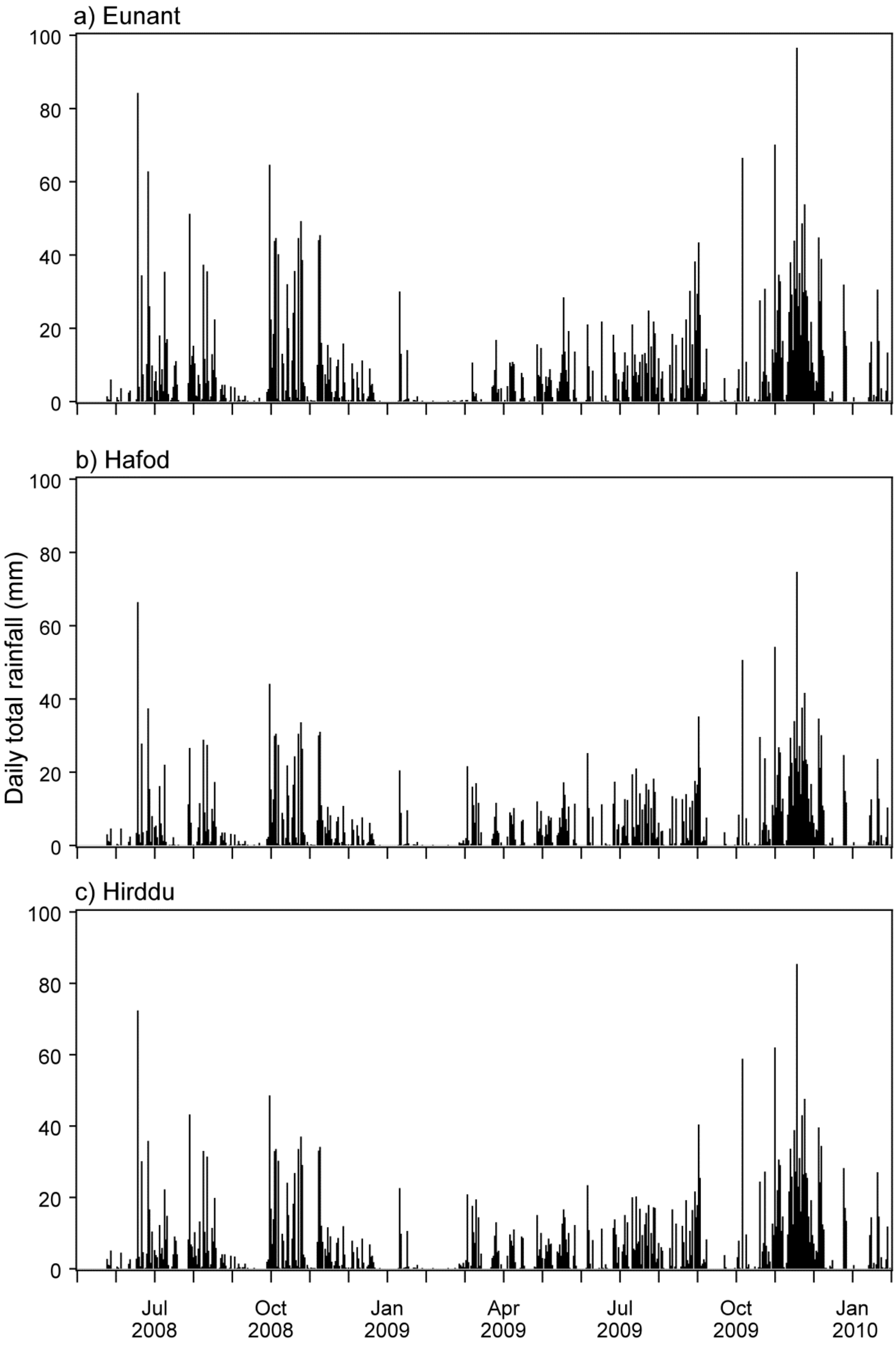

Fig. 3.11 Daily total rainfall (mm) from the Eunant, Hafod and Hirddu sites during May 2008 to January 2010.

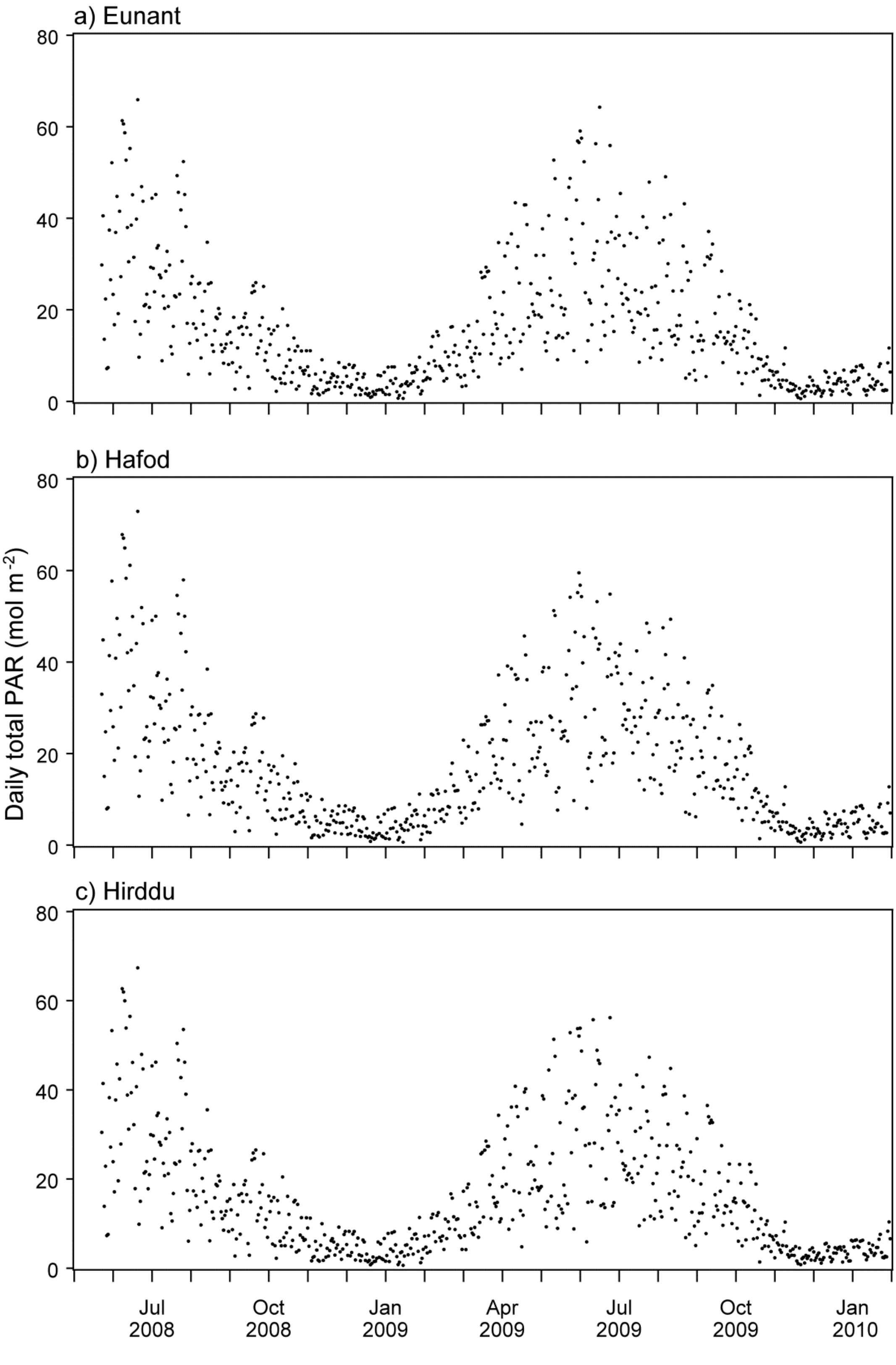

Fig. 3.12 Daily total PAR (mol m^{-2}) from the Eunant, Hafod and Hirddu sites during May 2008 to January 2010.

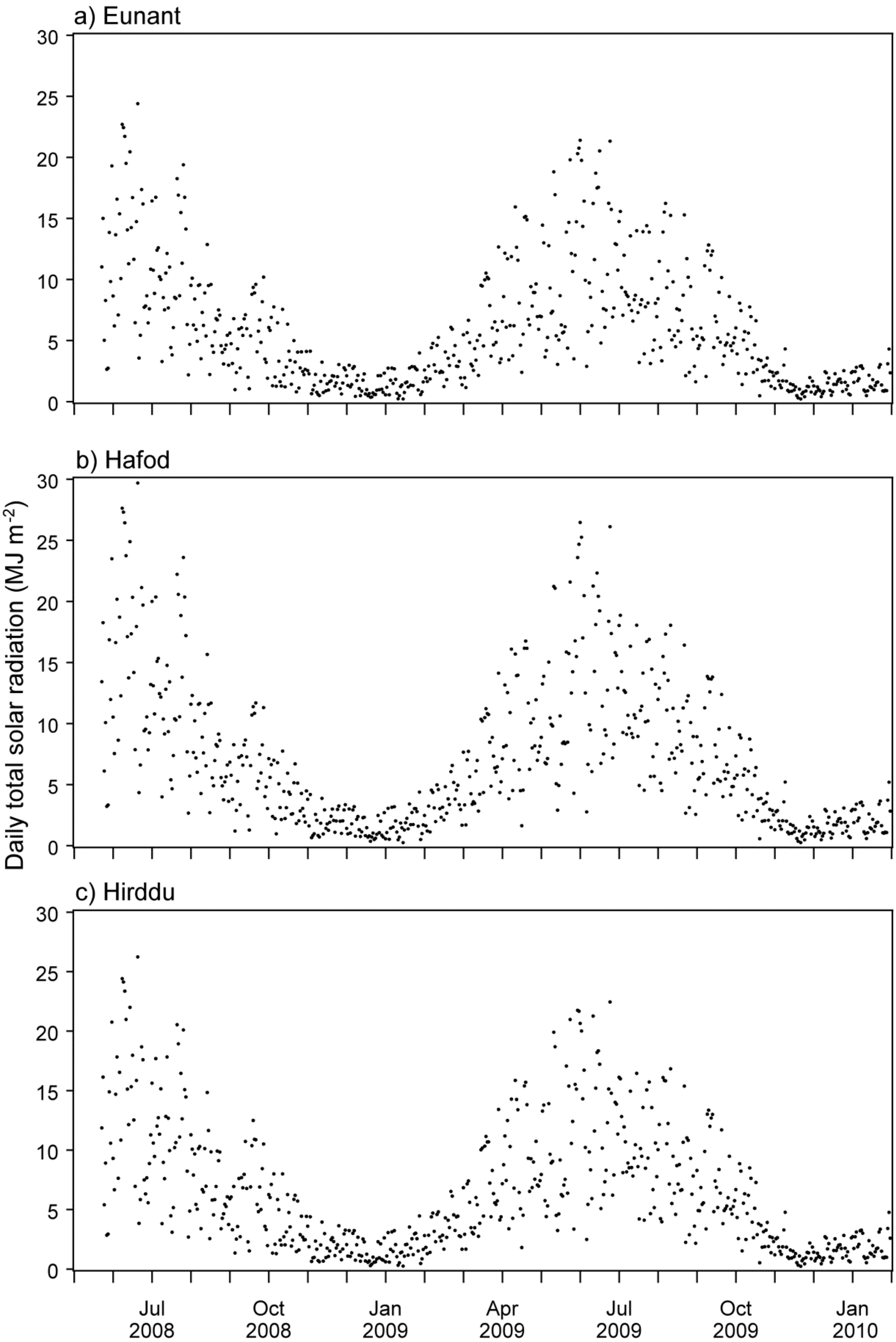

Fig. 3.13 Daily total solar radiation (MJ m^{-2}) from the Eunant, Hafod and Hirddu sites during May 2008 to January 2010.

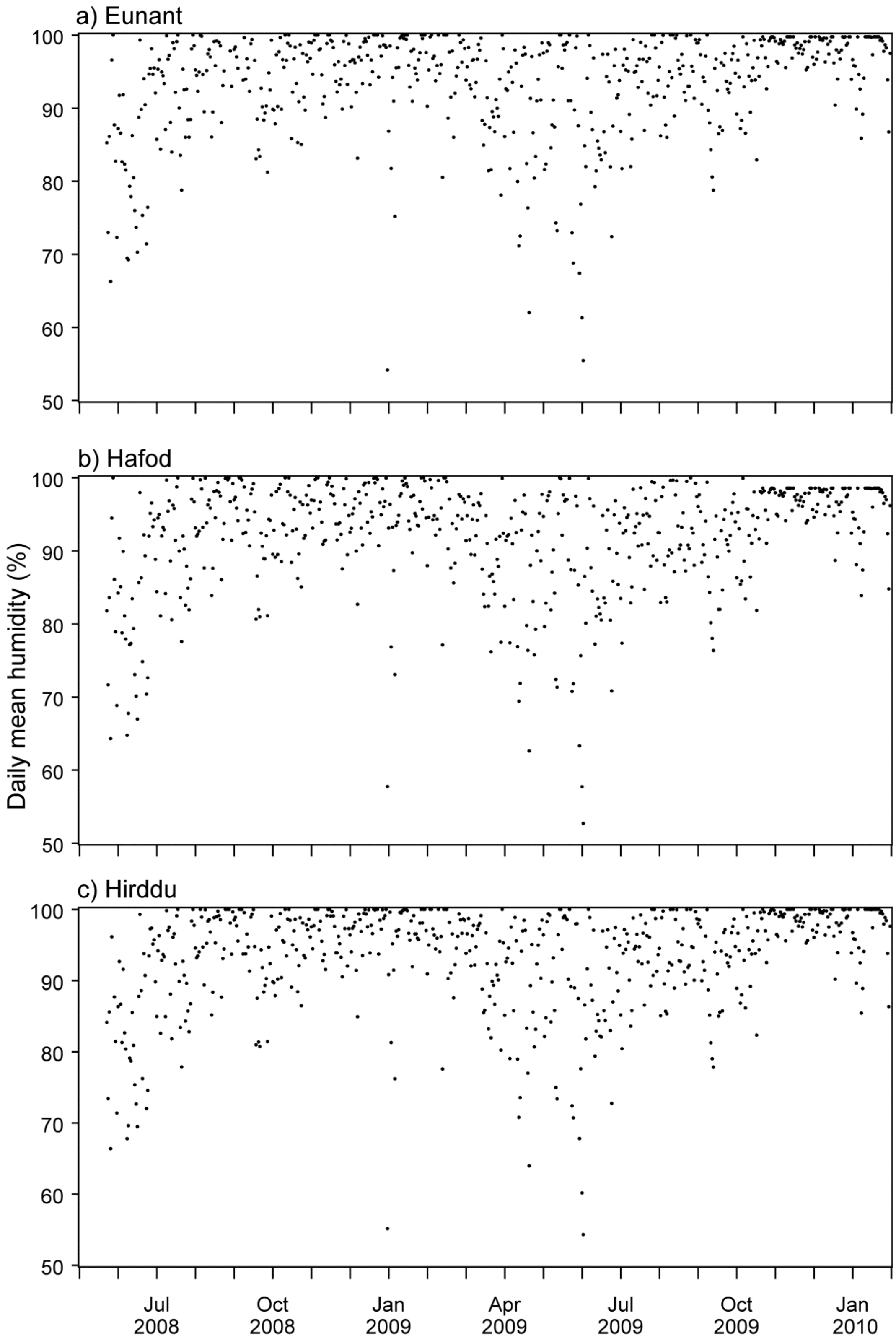

Fig. 3.14 Daily mean humidity (%) from the Eunant, Hafod and Hirddu sites during May 2008 to January 2010.

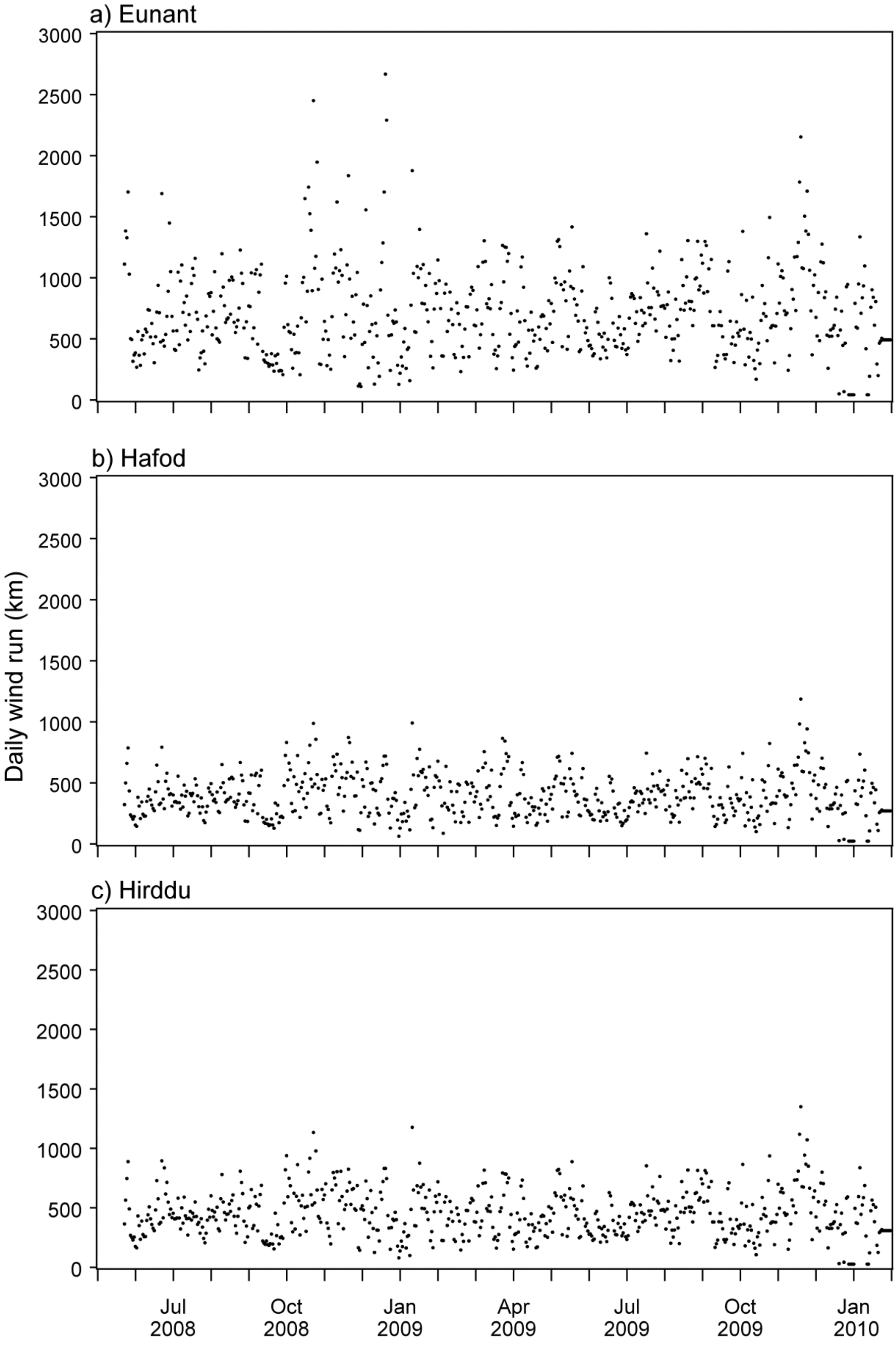

Fig. 3.15 Daily total wind run (km) from the Eunant, Hafod and Hirddu sites during May 2008 to January 2010.

3.3.1.2 Temperature

Annual mean soil temperatures at all sites and vegetation types had similar seasonal patterns, diverging between vegetation types during winter months, particularly during periods such as February 2009 and January 2010 when snow was observed on the ground. Another noticeable divergence between soil temperatures occurred from March to June 2009 at Eunant and Hafod when the Juncus soil temperature was warmer than all other vegetation types by around 1 °C. There was a significant difference between the 2009 annual mean soil temperature of each vegetation type (ANOVA, $p = 0.040$), and a *post hoc* Duncan's test showed that Juncus was significantly warmer than heather and sedge, but not grass (Fig. 3.16). Daily mean air temperatures from each site had very similar seasonal patterns to each other (Fig. 3.10) but differences existed between the annual mean air temperatures at each site; the annual mean air temperature during 2009 for Eunant, Hafod and Hirddu were 8.05 °C, 7.75 °C and 7.10 °C, respectively.

3.3.1.3 Other environmental variables

Daily total rainfall exhibited similar seasonal patterns at each site (Fig. 3.11); for all sites the driest period was during February 2009 and the wettest during November 2009. However, at 2398 mm, 1915 mm and 2151 mm for Eunant, Hafod and Hirddu, respectively, the total rainfall amounts during 2009 at each site varied considerably, the highest being 25% greater than the lowest. Both measures of radiation (daily total PAR and daily total solar radiation) had similar levels throughout the year at all sites with high variability during the summer, when low levels of radiation were still observed during some summer days (Fig. 3.12 and Fig. 3.13). During 2009, total PAR was 5954 mol m^{-2}, 6448 mol m^{-2} and 5961 mol m^{-2} and total solar radiation was 2178 MJ m^{-2}, 2571 MJ m^{-2} and 2351 MJ m^{-2} (or the yearly total solar radiation for 2009 was 604 kW h^{-1} m^{-2}, 714 kW h^{-1} m^{-2}, 652 kW h^{-1} m^{-2}), for Eunant, Hafod and Hirddu, respectively. A less pronounced seasonal pattern of humidity existed at all sites as humidity only reduced below 80% between April and July (Fig. 3.14).

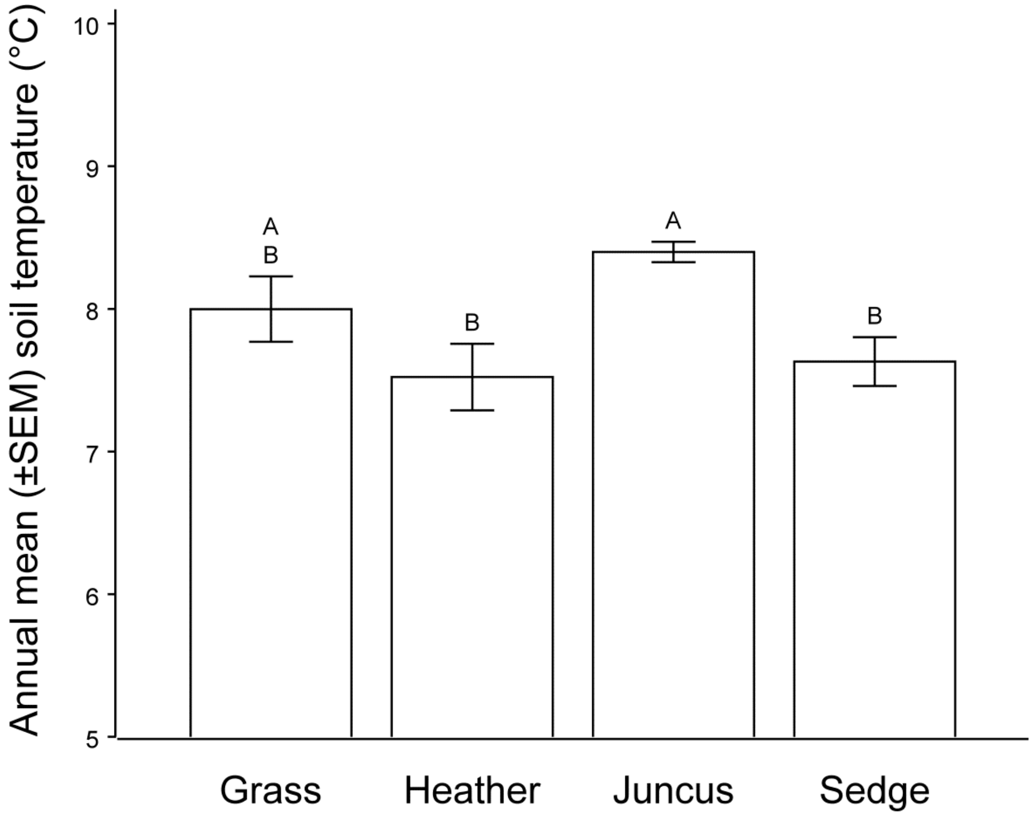

Fig. 3.16 Annual mean (± SEM) soil temperatures (°C) at a 10 cm depth from four vegetation types at all sites during 2009, n = 3. There was a significant effect of vegetation type on soil temperature ($p = 0.040$). Letters represent significant differences between vegetation types.

Annual mean values for each site during 2009 were 93.5% for Eunant, 91.7% for Hafod and 93.4% for Hirddu. There was no strong seasonal pattern for wind run measurements from any site, although the windiest days occurred at each site between October and January in 2008 and 2009 (Fig. 3.15). During 2009, the annual total wind run was 259720 km, 144175 km and 162782 km (or a mean wind speed of 8.24 m s^{-1}, 4.57 m s^{-1} and 5.16 m s^{-1}) for Eunant, Hafod and Hirddu, respectively. This considerable variation showed the windiest site, Eunant, was 80% windier than the least windy site, Hafod.

3.3.2 Multiple regression between CH_4 flux and concurrent environmental variables

In order to determine which environmental variables were controlling CH_4 fluxes measured throughout 2009, a series of regression models between fluxes and environmental variables were separately constructed for data from each vegetation type (where models which used data from heather vegetation types are referred to as heather models) and for all data, regardless of vegetation type. The initial approach was to use all environmental variables measured at the same time as fluxes (known as concurrent measurements) as independent variables in multiple stepwise regression models. As the positive skew of the distribution of CH_4 flux measurements suggested fluxes required transforming, separate models were constructed with untransformed and log_{10} transformed fluxes so that the effect of transformation could be identified. Results from models that used untransformed CH_4 fluxes showed that water table, soil temperature, air temperature and humidity were the only significant ($p<0.05$) independent variables selected at any step of the model-building process (Table 3.1). None of the eight independent variables could be significantly related to the CH_4 flux in the grass model. Depth to water table (r^2 = 0.141) was the only independent variable related to CH_4 flux in the heather model. Water table was also the first independent variable selected for the Juncus model and had a larger r^2 (0.244) than soil temperature (r^2 = 0.079), which was the only other significant independent variable explaining CH_4 flux. Water table was not significant at any step of the Sedge regression

Table 3.1 Results of multiple regressions between CH_4 flux and concurrent measurements of environmental variables for all data and for data subsetted by vegetation type (heather, Juncus and sedge; see text). The dependent variable (CH_4 flux) was either untransformed or log_{10} transformed. No significant regression models were produced for fluxes from grass vegetation.

Step and parameters	CH_4 flux				Log_{10} (CH_4 flux + 2.7)			
	Heather	Juncus	Sedge	All	Heather	Juncus	Sedge	All
First step								
Independent variable	Water table	Water table	Soil temp	Soil temp	Water table	Water table	Soil temp	Water table
β	0.049	-0.123	0.424	0.431	0.005	-0.013	0.031	-0.006
r^2	0.141	0.244	0.247	0.072	0.108	0.255	0.145	0.103
p	0.019	0.001	0.001	0.001	0.042	0.001	0.017	<0.001
Second step								
Independent variable		Soil temp	Humidity	Water table			Humidity	Soil temp
β		0.244	0.079	-0.056			0.007	0.039
r^2		0.079	0.168	0.086			0.178	0.030
p		0.047	0.003	<0.001			0.004	0.024
Third step								
Independent variable				Air temp				Air temp
β				-0.178				-0.021
r^2				0.049				0.070
p				0.003				0.001
Final model								
Intercept (β)	-0.247	1.784	-7.809	0.317	0.404	0.779	-0.197	0.509
r^2	0.141	0.323	0.415	0.206	0.108	0.255	0.329	0.202
p	0.019	0.001	<0.001	<0.001	0.042	0.001	0.001	<0.001

model, with soil temperature (r^2 = 0.247) and humidity (r^2 = 0.168) being the only significant independent variables. When all data were combined and used as the dependent variable in a single multiple regression model three environmental variables were significant: soil temperature (r^2 = 0.072), water table (r^2 = 0.078) and air temperature, which gave quite a weak final r^2 value of 0.204. The Juncus and sedge regression models which contained a much wider range of flux values (see Fig. 2.2 and Fig. 2.4) also had the highest r^2 values, with a maximum value of 0.415. In contrast, the grass and heather models with less variable fluxes produced lower r^2 values (0.141) or, in the case of the grass model, no significant regressions at all.

Table 3.1 also indicates that log_{10} transformation of fluxes did not have a consistent effect on r^2 values (and increased significance) for the multiple regressions between CH_4 fluxes and each environmental variable. The biggest change in regression due to logging the data occurred in the Juncus model as, despite an improvement of r^2 value for water table, soil temperature was no longer significant when transformed fluxes were used. This resulted in a reduction of r^2 for the final Juncus model from 0.323 to 0.255. The other notable impact of logging the data occurred in the model which used all data as the use of transformed fluxes, resulting in water table being the first selected independent variable, rather than soil temperature. Overall, final r^2 values of all models were marginally lower (0.202 compared to 0.206) when transformed flux data were used as dependent variables. The lack of improvement in final model r^2 led to the decision to use untransformed fluxes in the remaining models.

3.3.3 Single regression between CH_4 flux and the running averages of environmental variables

The next series of regression models used the running average of environmental variables over varying periods prior to the day of flux measurement as independent variables in order to identify the influence of environmental conditions over varying periods of time. This included average values from the same day of flux measurement (day 0) increasing up to seasonal averages over the preceding 180 days before the day of flux measurement (day 180). Single regression models were constructed for each environmental variable and the r^2 values produced by each regression model (that used running averages from 0 to 180 days) are shown on a single plot (see, for example, Fig. 3.17). Each plot shows all r^2 values for each combination of dependent (all data, or subsetted by vegetation type) and independent (soil temperature, air temperature, PAR, solar radiation, humidity, wind speed, rainfall and water table) variables. Fig. 3.17 and Fig. 3.18 show that r^2 values for all regressions increased to a greater or lesser extent when running averages were used as independent variables. As the period of running average prior to the day of flux measurement was extended, the r^2 from models of most combinations of variables steadily increased to a peak, followed by a reduction in r^2 value as the period of running average extended further. The progression in-to and out-of phase was most apparent for all measurements of temperature and radiation. The peak phase for soil temperature (a running average of between 32 and 74 days) was reached before air temperature (between 85 and 93 days) or PAR and solar radiation (which both peaked between 134 and 158 days). The peak phase for humidity did not appear to have been reached within a running average period of 180 days. In contrast, r^2 values from models which used water table appeared to decrease with the running average period, particularly for the heather models.

3.3.4 Multiple regression of CH_4 flux and the running averages of environmental variables

The final series of regression-based models utilised the running averages of several environmental measurements together as independent variables in a series of multiple regression models to explain the measured CH_4 flux data. Separate models were again constructed for fluxes from each vegetation type and for all data, regardless of vegetation

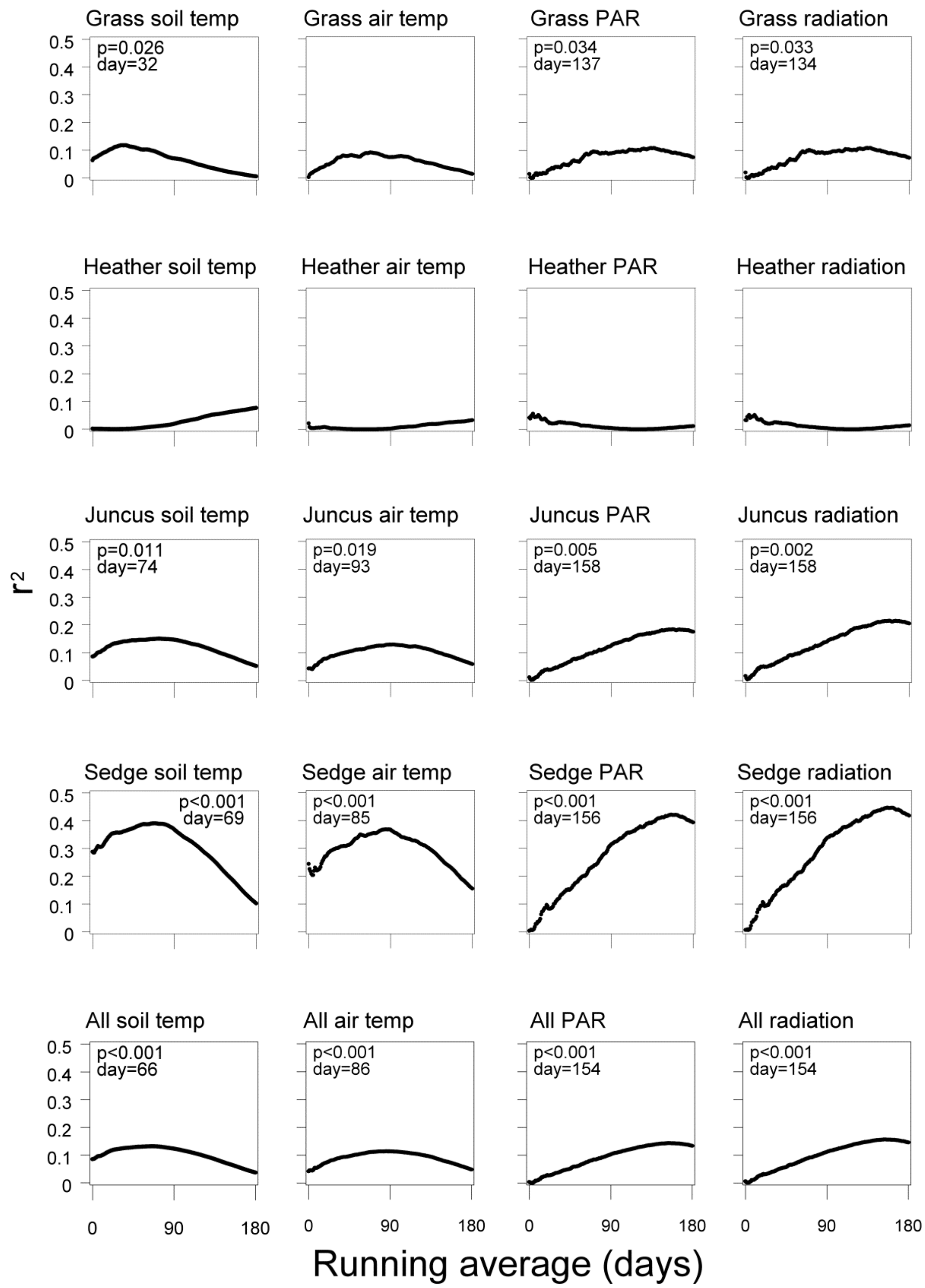

Fig. 3.17 Results (r^2 values) from a series of regression models between CH_4 fluxes of each vegetation type (dependent variable) and the running average of each environmental variable over 0 to 180 days prior to flux measurement (independent variable: soil temperature, air temperature, PAR and solar radiation). If significant, the most significant p value, and period of running average (day), are annotated on the plot.

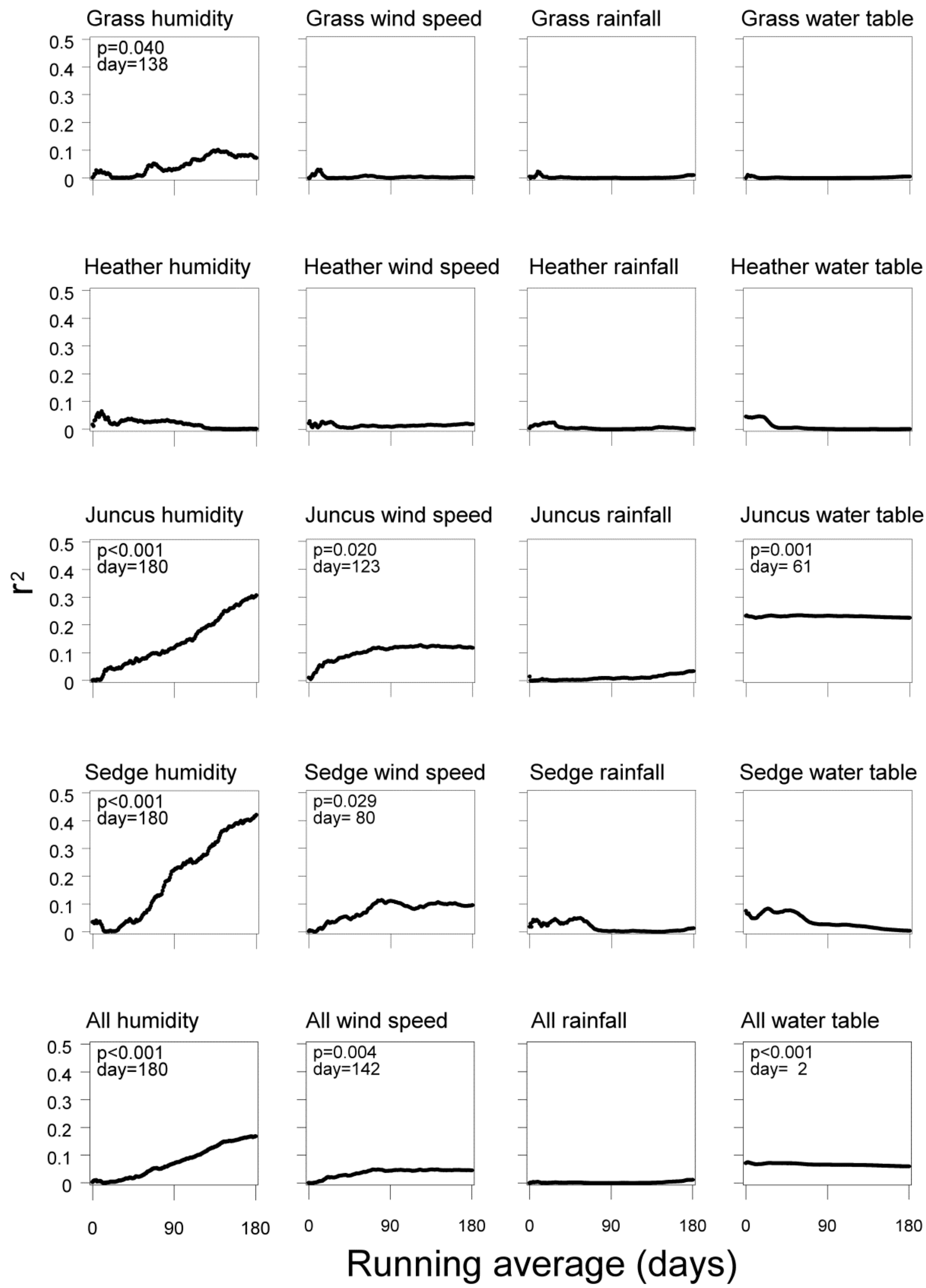

Fig. 3.18 Results (r^2 values) from a series of regression models between CH_4 fluxes of each vegetation type (dependent variable) and the running average of each environmental variable over 0 to 180 days prior to flux measurement (independent variable: humidity, wind speed, rainfall and water table; see Fig. 3.17).

type. As discussed in Section 3.2.3, not all environmental variables were used but soil temperature, solar radiation and water table were chosen as independent. Specifically, soil temperature and solar radiation were chosen since they had shown to be more significantly related to CH_4 than air temperature and PAR, respectively (Table 3.1 and Fig. 3.17) and water table is shown in other studies to be significantly related to CH_4 flux (see, for example, Bubier *et al.* 2005). The use of running averages from just three environmental variables, varying over 0 to 180 days prior to the day of flux measurement, resulted in ca. six million possible regression models for each vegetation type which restricts how results can be presented.

Results are shown here initially from models which use just two environmental variables: soil temperature and solar radiation. The results from all regression models for each vegetation type are shown on a single plot, with r^2 values shown as a response variable to the change in running average period for both environmental variables (Fig. 3.19 to Fig. 3.21). In order to show results clearly, r^2 values are grouped into coloured classes, with blue indicating models with low r^2 and red indicating models with relatively high r^2 values. Any non-significant regression models are not included in any class, and are subsequently left blank on each plot. Results are first presented from each pair of environmental variables, specifically, soil temperature and solar radiation (Fig. 3.19), soil temperature and water table (Fig. 3.20), and solar radiation and water table (Fig. 3.21). Results are then shown from models which use all three environmental variables. No results from attempts to explain heather fluxes are included in this section as all regression models were non-significant.

3.3.4.1 Soil temperature and solar radiation

The use of running averages of soil temperature and solar radiation in the grass models (Fig. 3.19a) revealed that neither variables were significant in the same model, regardless of

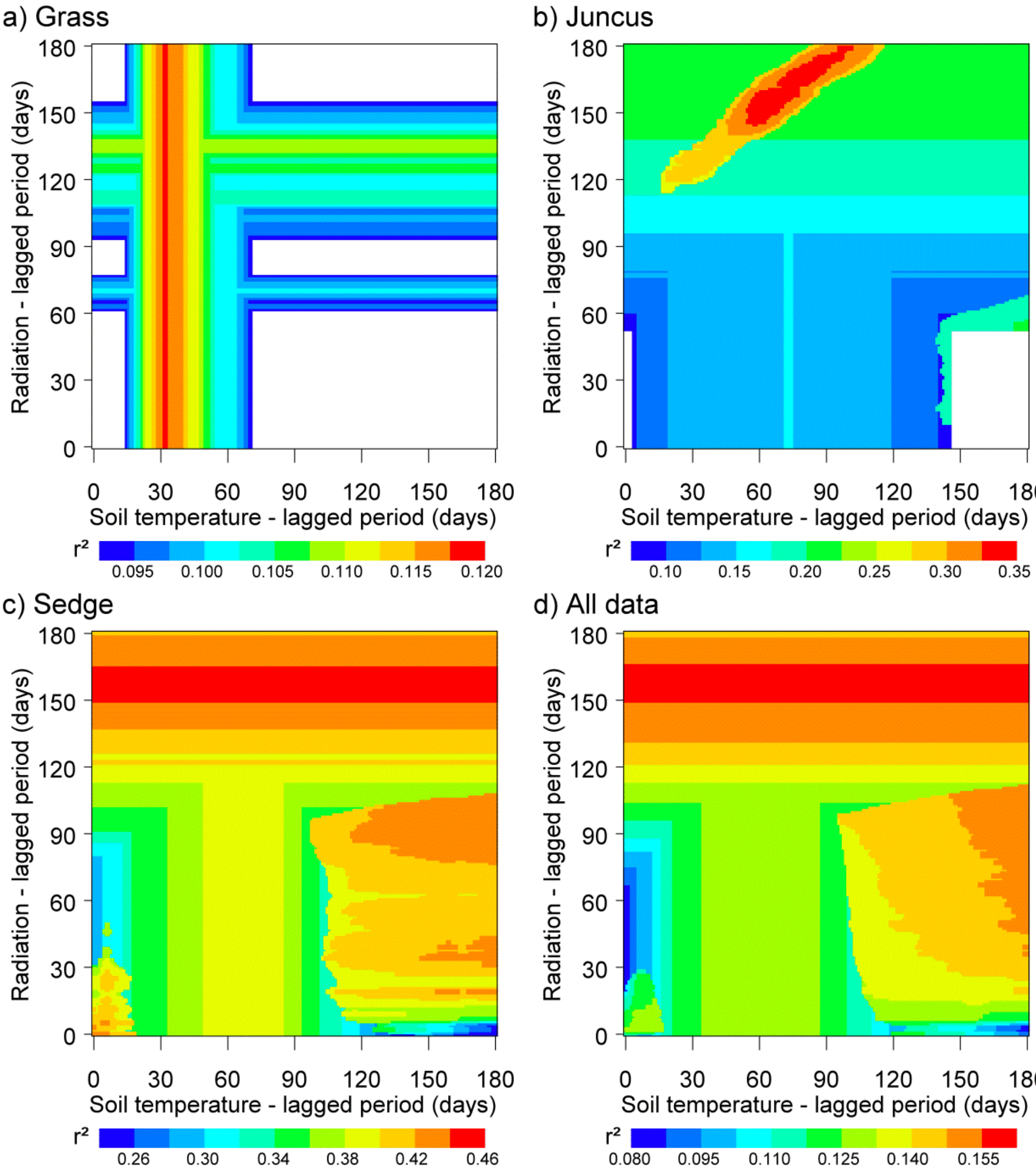

Fig. 3.19 Results (r^2, represented by response value) from a series of multiple regression models between CH_4 flux (dependent variable) and the running average of soil temperature and solar radiation over 0 to 180 days prior to flux measurement. Blank response values represent non-significant models. Subsets of data from grass (a), Juncus (b) and (c) sedge and data from all vegetation types (d) are shown. Heather models using all combinations of running averages used in the heather models were non-significant.

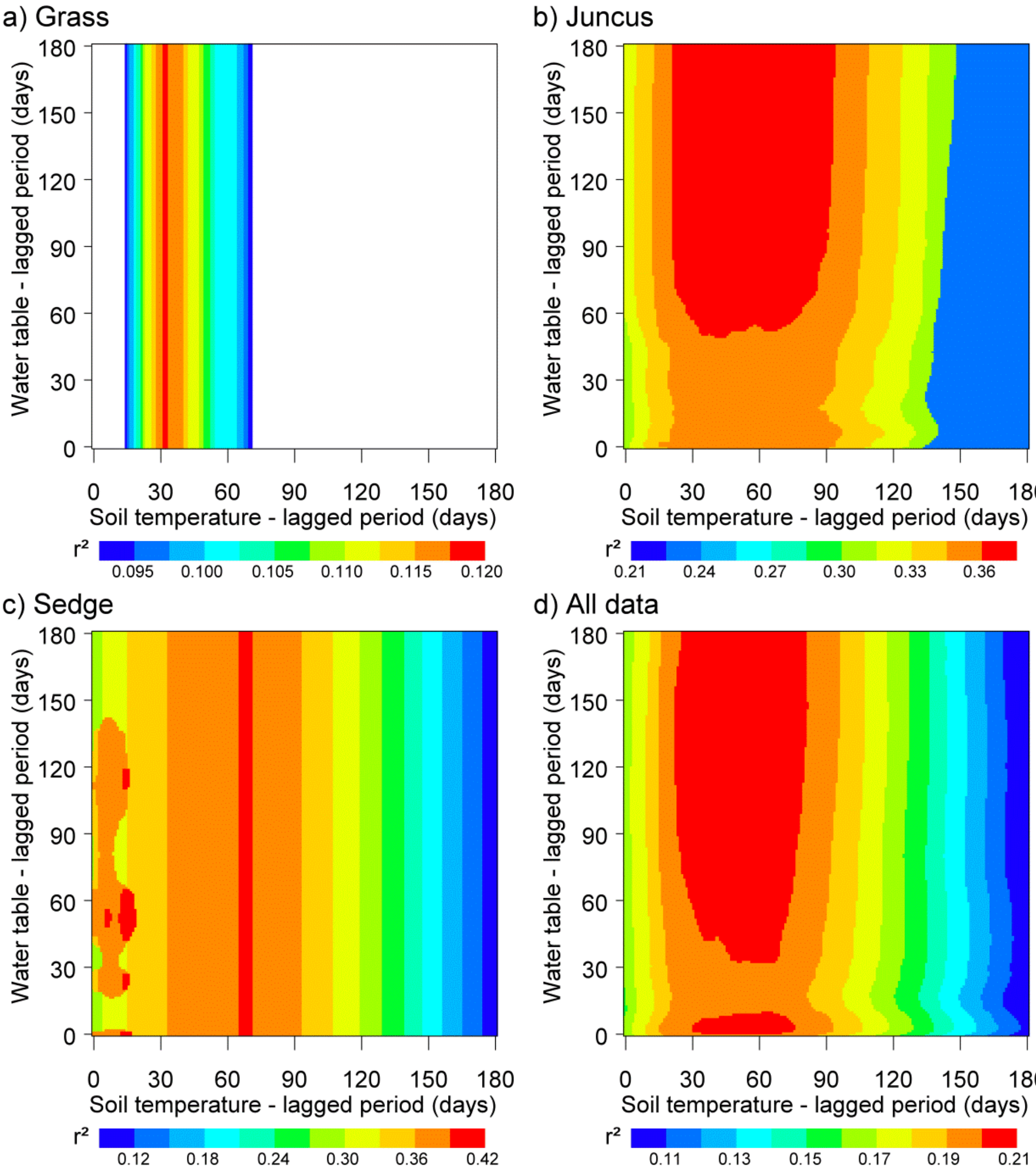

Fig. 3.20 Results (r^2, represented by response value) from a series of multiple regression models between CH_4 flux (dependent variable) and the running average of soil temperature and depth to water table over 0 to 180 days prior to flux measurement (see Fig. 3.19).

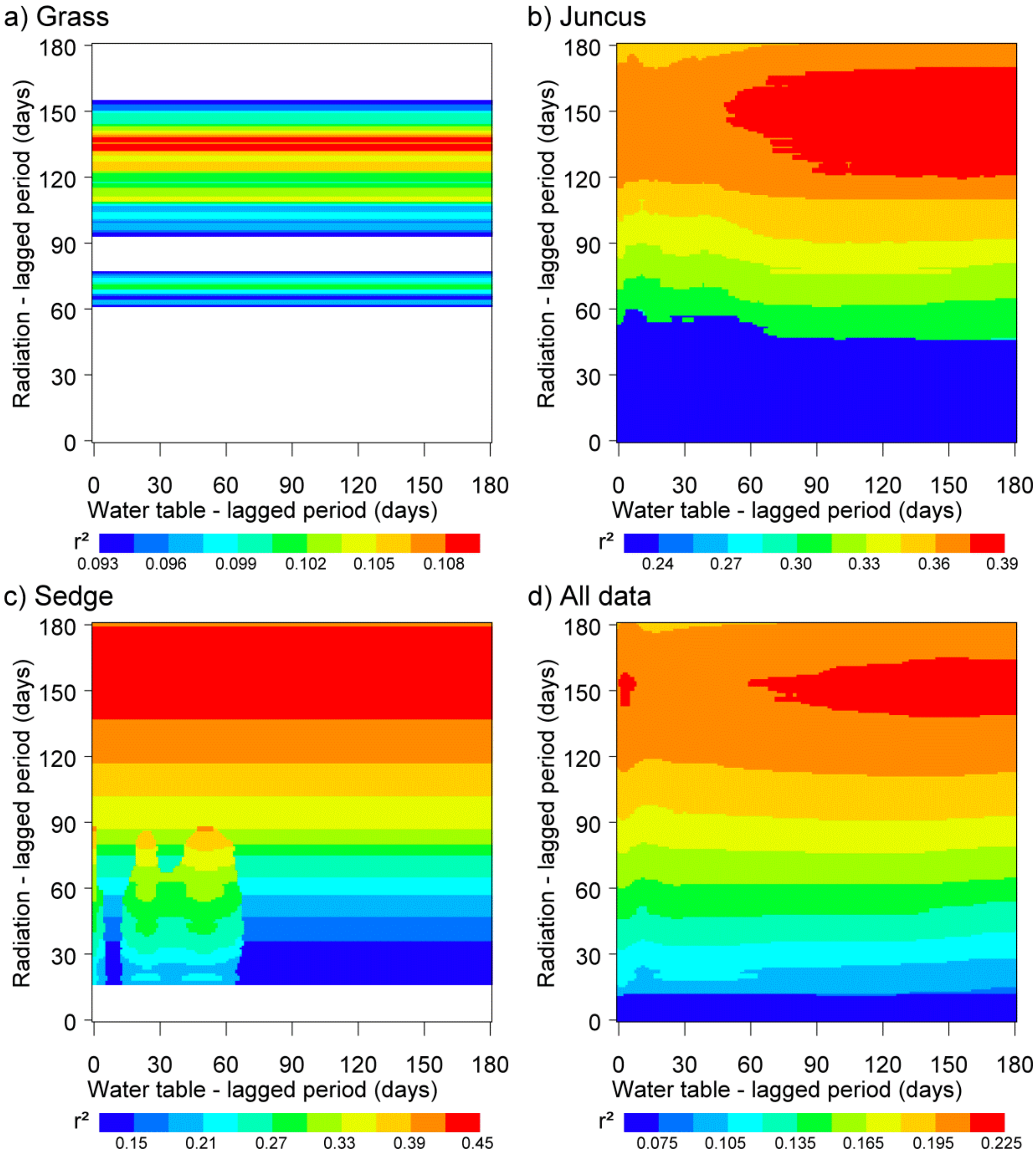

Fig. 3.21 Results (r^2, represented by response value) from a series of multiple regression models between CH_4 flux (dependent variable) and the running average of depth to water table and solar radiation over 0 to 180 days prior to flux measurement (see Fig. 3.19).

the combination of running average periods used. Effectively, the straight vertical lines which peaked around 32 days and the straight horizontal lines which peaked around 134 days were the same individual results produced for soil temperature and solar radiation in the series of single regression models (Fig. 3.17) and there is no additional explanation produced from combining these variables in a single model. In contrast, the results from the Juncus models (Fig. 3.19b) revealed a distinctive area of the plot, stretching diagonally between ca. 50 to 100 days for soil temperature and ca. 140 to 180 days for solar radiation, where r^2 values show an interaction between soil temperature and solar radiation. The interaction is a result of both environmental variables being significant in all the regression models represented in this non-linear pattern.

The absence of blank r^2 values in the results from the sedge models (Fig. 3.19c) shows that all models were significant. In addition, two areas of interaction are visible: one between ca. 0 to 15 days for soil temperature and ca. 0 to 30 days for solar radiation, and the second, larger area between ca. 120 to 180 days for soil temperature and ca. 5 to 105 days for solar radiation. However, unlike the Juncus models, the highest r^2 values from the sedge models (horizontal lines around 150 days) were no higher than from the series of single regression models (Fig. 3.19d). Results for models which used all data were very similar to those from the sedge models, with the exception that r^2 values were considerably lower.

3.3.4.2 Soil temperature and water table

Water table was not significant in any of the grass models that used soil temperature and water table as independent variables. This resulted in the straight vertical lines and absence of interaction seen in Fig. 3.20a. In contrast, as soil temperature and water table were both significant in all Juncus models, there were no strict linear patterns in Fig. 3.20b, regardless of the combination of running averages used. The dominant pattern of straight vertical lines in Fig. 3.20c indicates that soil temperature was significant in all sedge models. However, water table was also significant in a number of models when the running average of soil temperature was between 0 and 18 days.

The results from this series of models which used data from all vegetation types show similar results to the Juncus models as soil temperature and water table were both significant in all models (Fig. 3.20d). The one notable difference, however, was a pattern of higher r^2 values observed when the running average period for soil temperature and water table was ca. 30 to 75, and ca. 0 to 10 days, respectively. An interaction between soil temperature and water table was also not observed in this area for the grass or sedge models, either. Rather, this reflected the increased r^2 values observed in the series of single regression models for heather that used running averages (Fig. 3.18).

3.3.4.3 Water table and solar radiation

As when used with soil temperature, water table was again not significant in any of the grass models that used water table and solar radiation as independent variables (Fig. 3.21a). As before, the absence of strict linear patterns in Fig. 3.21b, indicates that both solar radiation and water table were significant in all Juncus models. Solar radiation was the only significant independent variable in most of the sedge models (see Fig. 3.21c). However exceptions to this occurred when (1) the models were not significant, as indicated by the blank r^2 values when the running average period of solar radiation was less than 17 days; and (2) when water table was also significant, as indicated by a pattern of interaction between ca. 0 to 60 days for water table and 17 to ca. 90 days for solar radiation.

Water table and solar radiation were both significant independent variables in all models which used data from all vegetation types (Fig. 3.21d). The results showed similar patterns to the results from the sedge models, and again showed an additional area of high r^2 values when water table was less than ca 10 days.

3.3.4.4 *Soil temperature, solar radiation and water table*

The following results are all from models which used the three variables soil temperature, solar radiation and water as independent variables, each represented by a running average over a period of between 0 (the day of the flux measurement) and 180 days (an average over the preceding 180 days prior to the flux measurement). Again, presentation of the resulting r^2 from each of ca. 6 million different regression models is problematic and is also compounded by the problem of plotting all three of the contributing variables. This has been achieved by constructing plots which included r^2 values from the running average of soil temperature on the x-axis, solar radiation on the y-axis and were repeated for each value (0 to 180 days) of water table along an unseen z-axis. All 181 plots for each running average of water table are not presented here; rather a selection of nine plots each representing a different running average periods of water table (see, for example, Fig. 3.22 to Fig. 3.24). Each series of results were selected as those which best represented the changing patterns of regression model r^2 throughout the entire range of running averages of water table. Water table was not significant in any of the grass models that used soil temperature, solar radiation and water table and are consequently not shown as they were identical to Fig. 3.19a.

The series of results from the Juncus models (Fig. 3.22) retained some of the patterns produced when only soil temperature and solar radiation were used in each model (see Fig. 3.19b). However, the inclusion of water table which was significant in all models removed the interaction, seen as a diagonal non-linear pattern, between soil temperature and solar radiation (Fig. 3.19b). As the running average period of water table was increased above day 0, r^2 values around 150 days of radiation and 45 days of soil temperature decreased from their initial level to a minimum at day 17 (Fig. 3.22b). From day 17, r^2 values across large areas of the plots increased consistently up to a maximum at day 170 (Fig. 3.22c to h). All three environmental variables were significant when the running average period of

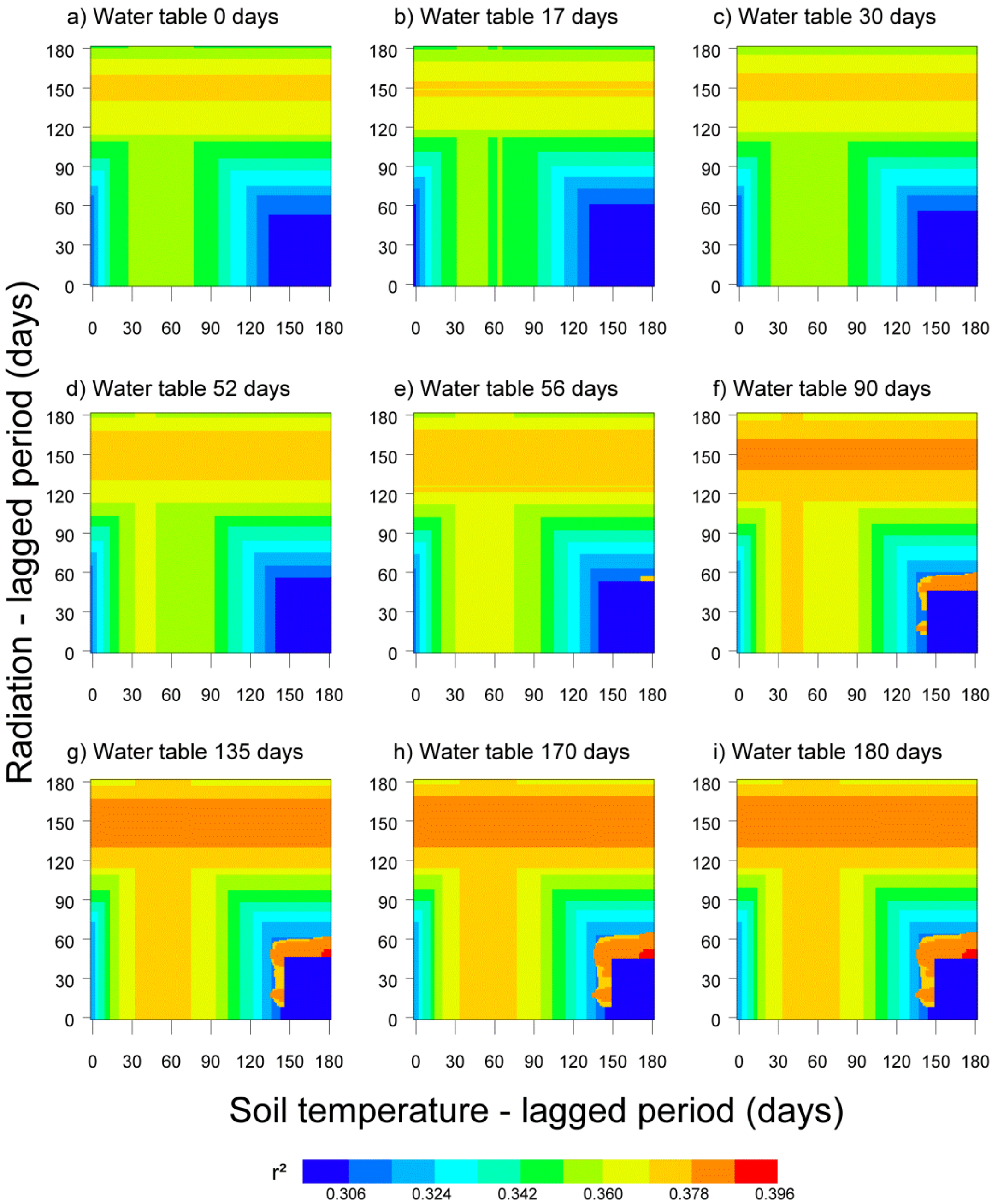

Fig. 3.22 Results (r^2, represented by response value) for Juncus vegetation from a series of multiple regression models between CH_4 flux (dependent variable) and the running average measurements of soil temperature, solar radiation and depth to water table over 0 to 180 days prior to the day of flux measurements. A series of results are shown (a to i) as the running average period of depth to water table changes from 0 days to 180 days.

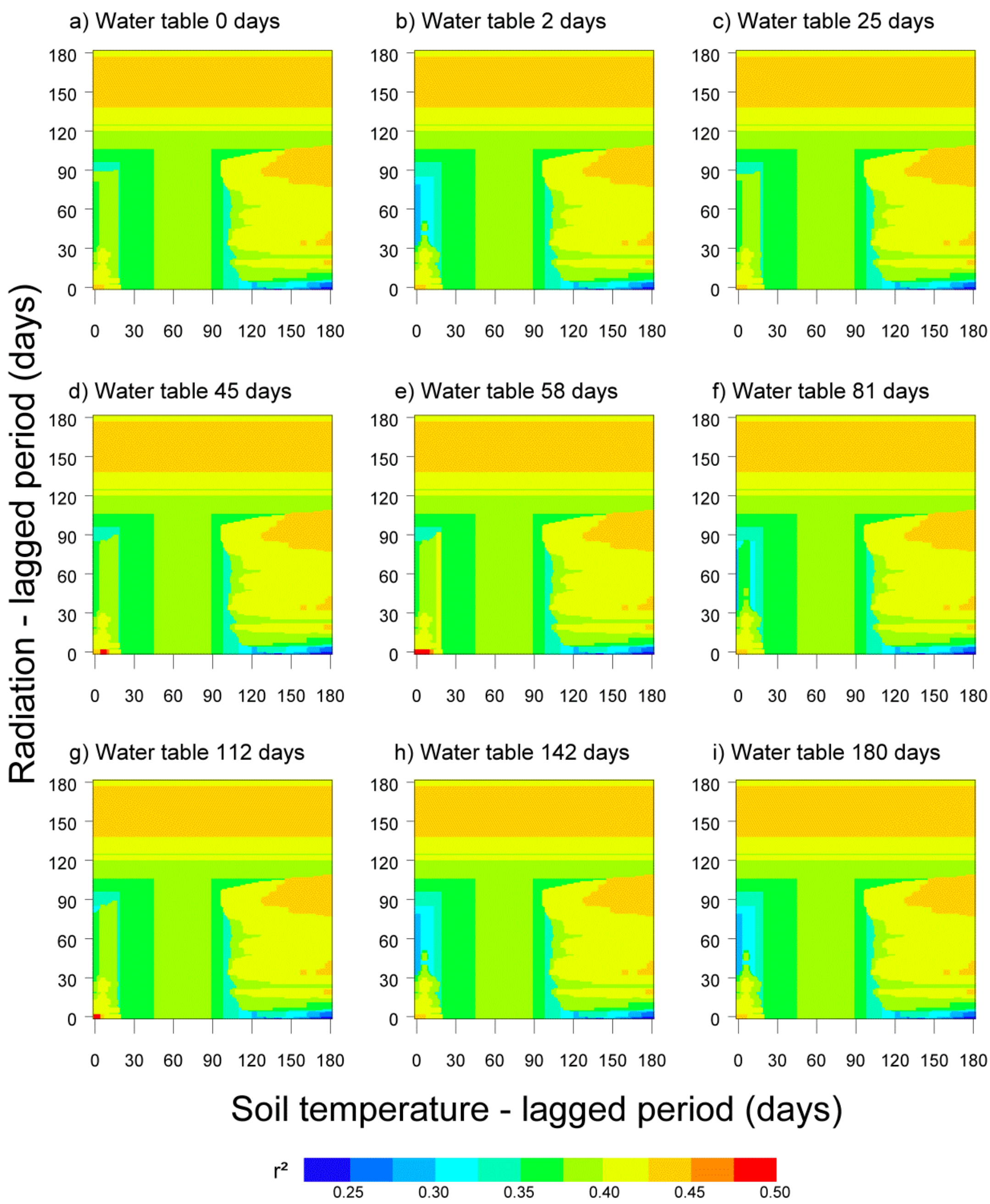

Fig. 3.23 Results (r^2, represented by response value) for sedge vegetation from a series of multiple regression models between CH_4 flux (dependent variable) and the running average measurements of soil temperature, solar radiation and depth to water table over 0 to 180 days prior to the day of flux measurements. A series of results are shown (a to i) as the running average period of depth to water table changes from 0 days to 180 days.

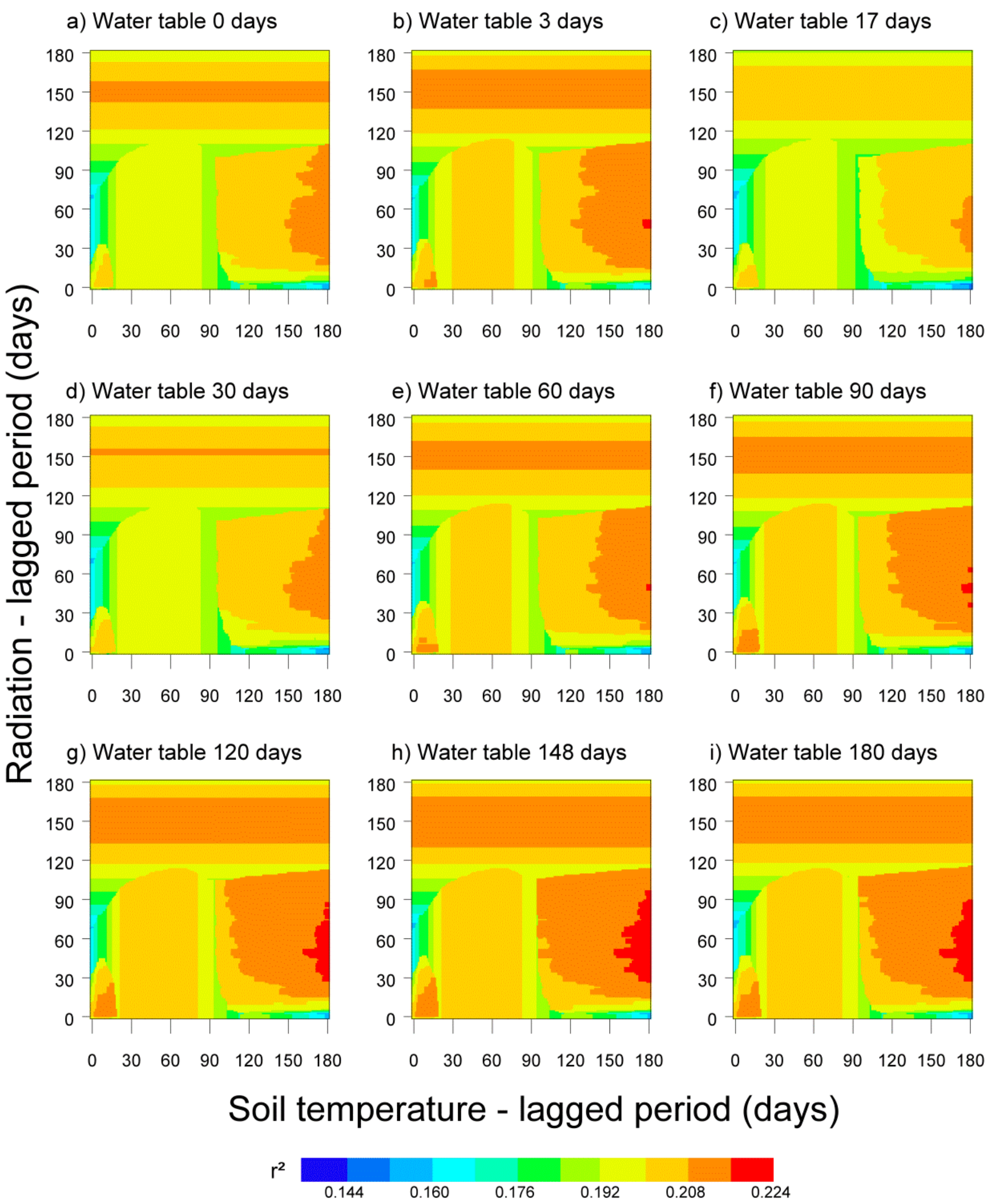

Fig. 3.24 Results (r^2, represented by response value) for data from all vegetation types from a series of multiple regression models between CH_4 flux (dependent variable) and the running average measurements of soil temperature, solar radiation and depth to water table over 0 to 180 days prior to the day of flux measurements. A series of results are shown (a to i) as the running average period of depth to water table changes from 0 days to 180 days.

water table was 56 days and higher (Fig. 3.22e to i). This interaction between all three variables was centred on an area when the running average of soil temperature and solar radiation was ca. 180 and 45 days, respectively, as can be seen by the changing area of interaction in Fig. 3.22e to i.

The series of results from the sedge models (Fig. 3.23) also showed similar patterns as the sedge models which only used soil temperature and solar radiation as independent variables (Fig. 3.19c). These features included high r^2 values when the running average of solar radiation was around 150 days, and two areas of interaction. Water table was significant in a single area of the plots where the running average of soil temperature and solar radiation was ca. 0 to 15 and ca. 0 to 90 days, respectively. Consequently, this was the only area which contained an interaction between all three variables. Water table was significant in this area when its running average period was between 0 and 141 days and r^2 values increased and decreased over this period in a similar manner to the pattern seen when only soil temperature and water table were used (Fig. 3.20c). Specifically, areas of high r^2 values were at their largest on days 2, 45 to 58, and around 112, but at their smallest on days 25 and 81.

The series of results from models which used all vegetation types (Fig. 3.24) showed similar patterns to the corresponding regression models which did not include water table (Fig. 3.19d). Water table was significant in all models, so patterns changed across wide areas of the plots as the running average period for the water table increased. However, changes in all areas followed a similar progression as the running average of water table increased. This included areas of high r^2 values which were at their largest at day 3, reducing until day 17, after which they steadily increased up to day 148. Whilst the general pattern of plots is similar to results from the sedge models (Fig. 3.23), the area of highest r^2 values is in a similar location as that observed in the results from the Juncus models (Fig. 3.22).

3.3.5 Regression results summary

By changing independent variables used in the model for each vegetation type it was possible to compare how different models produced the varying maximum r^2 values and altered which environmental variables were significant (Table 3.2). The use of running averages in single regression models produced a varied response of maximum r^2 dependent on which vegetation type was used. A positive effect was observed for grass and sedge, but a lower maximum r^2 was produced for heather and Juncus. The subsequent use of running averages in multiple regression models meant that, with the exception of heather, final r^2 values were higher than when simply derived from the use concurrent measurements alone, but r^2 values were never higher than 0.5.

3.3.6 Impact of ditch blocking on CH_4 flux

Out of 300 individual flux measurements, 214 (71.3%) CH_4 fluxes were accepted by the flux algorithm and all combinations of management technique, vegetation, elevation, and season (where season represents the different month and year that fluxes were measured) were represented. Measurements were averaged to produce a single measured CH_4 flux for each combination of factors. The mean (±SEM) CH_4 flux of heather sites in March 2009, regardless of other factors, was -0.132 (±0.079) mg CH_4 m^{-2} h^{-1}, compared to -0.219 (±0.032) mg CH_4 m^{-2} h^{-1} for heather vegetation during March of the seasonal study in 2009 (see Fig. 2.2). Similarly, the mean (±SEM) CH_4 flux from/to sedge sites in March 2009 and August 2010 were -0.0534 (±0.088) and 0.212 (±0.436) mg CH_4 m^{-2} h^{-1}, respectively, compared to 0.280 (±0.338) and 6.886 (±1.651) mg CH_4 m^{-2} h^{-1} during March and August of the 2009 seasonal study.

The first analysis of data collected during March, 2009 (see Fig. 3.25) controlled for both vegetation and elevation and showed that ditch blocking did not appear to have a significant effect on CH_4 fluxes (Friedman's ANOVA, $p = 0.827$). The test was repeated twice

Table 3.2 Maximum r^2 values achieved from each approach used in the regression modelling between CH_4 flux and environmental variables for data from each vegetation type, and all data combined. Approaches used (i) concurrent environmental variables in multiple regressions, (ii) running averages of environmental variables in periods varying from 0 to 180 days prior to the day of flux measurement in single regression models, and (iii) running averages of soil temperature, solar radiation and water table (from 0 to 180 days) in multiple regressions. Results that were not significant are indicated by n/s.

Vegetation type	Environmental variables input		
	Multiple concurrent	**Single running average**	**Multiple running average**
Grass	n/s	Soil temp. (32 days); 0.118	Soil temp. (32 days); 0.118
Heather	Water table; 0.141	n/s	n/s
Juncus	Water table & soil temp.; 0.323	Humidity (180 days); 0.307	Water table (170 days) & solar radiation (47 days) & soil temp. (180 days); 0.390
Sedge	Soil temp. & humidity; 0.415	Solar radiation (156 days); 0.446	Soil temp. (0 days) & solar radiation (0 days) & water table (58 days); 0.493
All	Soil temp & water table & air temp.; 0.206	Humidity (180 days); 0.168	Soil temp. (180 days) & solar radiation (50 days) & water table (148 days); 0.221

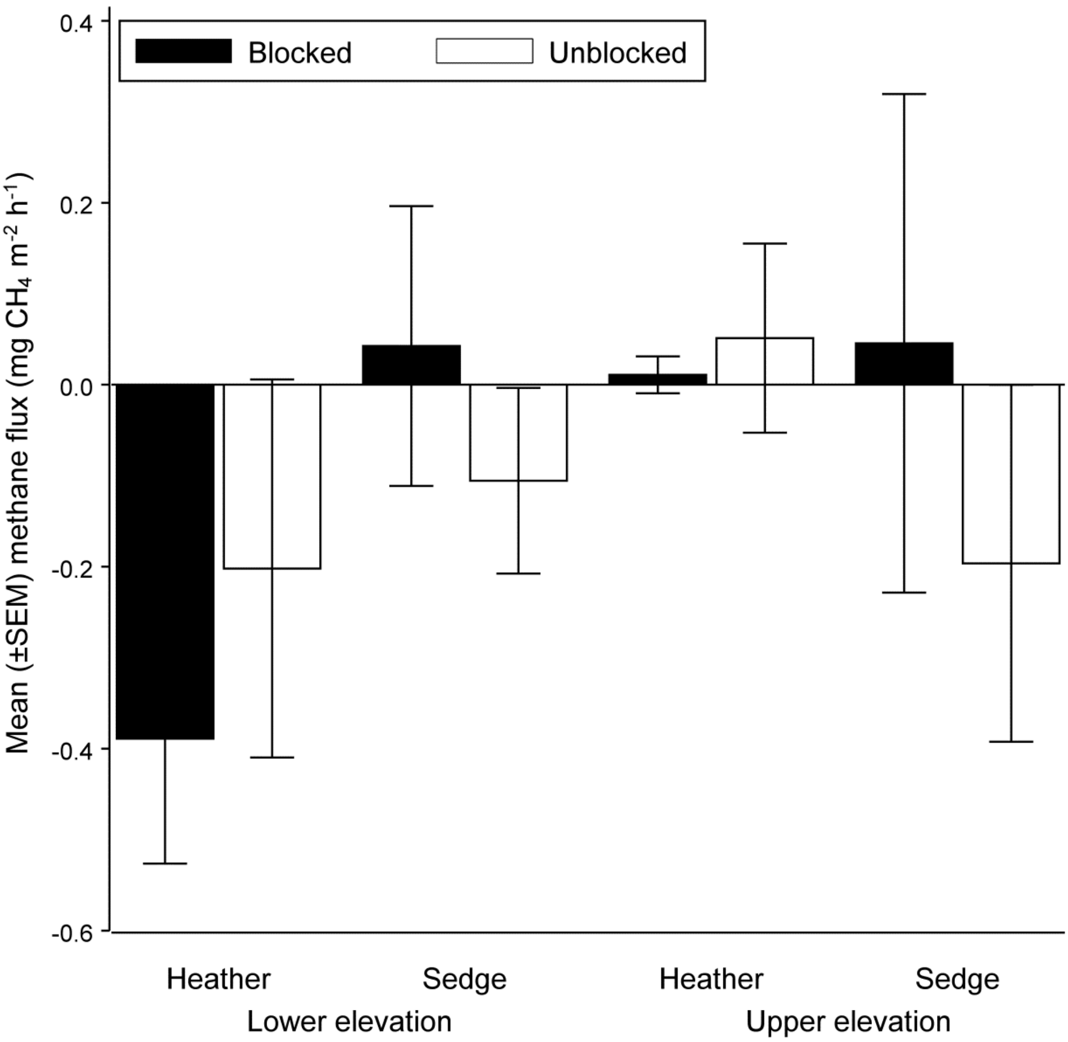

Fig. 3.25 Mean (±SEM) CH_4 flux (mg CH_4 m^{-2} h^{-1}) of different management techniques (blocked and unblocked drains), vegetation (heather and sedge) and elevation (lower (470-475 m.a.s.l.) and upper (520 - 525 m.a.s.l.)). After controlling for vegetation and elevation, management technique did not have a significant effect on CH_4 fluxes (Friedman's ANOVA, $\chi^2(1) = 0.05$, $p = 0.827$), n = 3.

to separately examine the effect of vegetation, whilst controlling for elevation and ditch blocking, and the effect of elevation, whilst controlling for vegetation and ditch blocking. Results showed no significant effect of either vegetation ($p = 0.663$) or elevation ($p = 0.190$) on CH_4 fluxes.

The final analyses of data focused on the sedge vegetation at lower elevations only, but included CH_4 measurements from March 2009 and August 2010 (see Fig. 3.26). After controlling for season and vegetation, ditch blocking did not appear to have a significant effect on CH_4 fluxes (Friedman's ANOVA, $p = 0.758$). When this test was repeated, but controlling for ditch blocking, there was also no significant effect of season on CH_4 fluxes ($p = 0.355$).

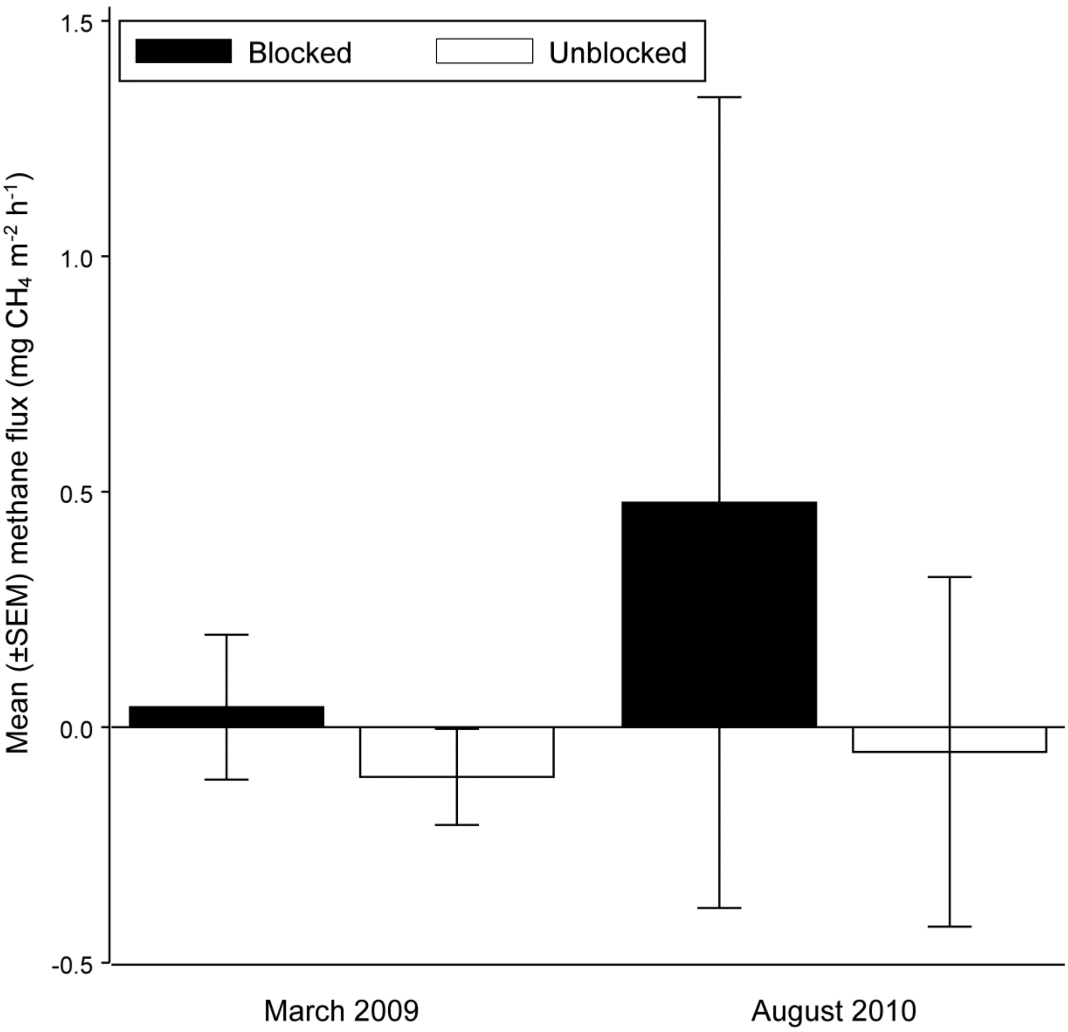

Fig. 3.26 Mean (±SEM) CH_4 flux (mg CH_4 m^{-2} h^{-1}) of different management techniques (blocked and unblocked drains), and season (March 2009 and August 2010). After controlling for season and vegetation, management technique did not have a significant effect on CH_4 fluxes (Friedman's ANOVA, $\chi^2(1) = 0.09$, $p = 0.758$), n = 3.

3.4 Discussion

3.4.1 Environmental conditions

With average air temperature of 8.05 °C, 7.75 °C and 7.10 °C, respectively, the Eunant, Hafod and Hirddu sites were all warmer during 2009 than the average air temperature during 1961-1990 at a location with a similar elevation less than 4 km from all sites (Afon Eiddew; see Fig. 2.1), which was 6.4 °C (Freitag *et al.* 2010). In addition, all sites received more rainfall during 2009 than the average during 1961-1990 (also at Afon Eiddew), which was 1501 mm (Freitag *et al.* 2010); the Eunant site received 2398 mm, which was also considerably more than the amount received at both the Hafod (1915 mm) and Hirddu (2151 mm) sites. During 2009, the Eunant site was also much windier (259720 km; total wind run see Section 3.2.2) than either Hafod (144175 km) or Hirddu (162782 km), a difference which was most likely a result of its higher elevation of 546 m, compared to 473 and 508 m for Hafod and Hirddu, and closer proximity to the steep-sided valleys to the west of the study site (Fig. 2.1). Comparison between vegetation types showed that soils at Juncus sites were significantly warmer than heather and sedge sites during 2009, and that water table was significantly deeper from the surface at grass sites than at heather and sedge (Fig. 3.3).

The considerable differences in environmental conditions between meteorological stations, which were a maximum of 4 km apart, and significant differences between vegetation types, which were a maximum of 40 m apart but generally about 10 m apart at each site, demonstrates the small-scale variation which existed in this heterogeneous site. Similar studies of peatlands also provide evidence of significant small-scale heterogeneity in environmental conditions such as soil temperature and water table (McNamara *et al.* 2008; Dinsmore *et al.* 2009a). Temperature (for example, see Christensen *et al.* 2003) and water table (for example, see Bubier *et al.* 1993) have been shown to be important controls of

CH_4 fluxes in peatlands but small-scale spatial variations of environmental conditions are typically neglected in studies of CH_4 fluxes made at a large spatial scale (such as Walter *et al.* 2001a; Bloom *et al.* 2010b). The impact of ignoring small-scale variation has the potential to miss relatively high proportions of overall flux as they may occur in spatially limited (Saarnio *et al.* 1997; Becker *et al.* 2008; Schrier-Uijl *et al.* 2010; Teh *et al.* 2011) or temporally limited points (Mastepanov *et al.* 2008). Walter *et al.* (2001b) tested the impact of ignoring microtopographical variations in water table across wetlands in a 1° by 1° grid cell, a variation they suggest is linked to differences in elevation and vegetation coverage. The inclusion of a simple assumption, that 10% of the wetland area in each cell is permanently flooded, 30% is permanently dry enough to stop all CH_4 emissions and 60% has the cell's mean water table, appears to improve CH_4 flux predictions in northerly latitudes and indicates that the *a priori* assumption that water table is constant at such large scales reduces the ability of such models to accurately predict CH_4 fluxes.

3.4.2 Environmental controls on CH_4 fluxes

Concurrent soil temperature or water table were found to be significant controllers of CH_4 fluxes from all vegetation types except grass (Table 3.1). This result is well supported by a large variety of studies which also found CH_4 fluxes to be controlled by soil temperature and water table at sites in the UK (for example, see McNamara *et al.* 2008; or Dinsmore *et al.* 2009a), Scandinavia (for example, see Christensen *et al.* 2003), Siberia (for example, see Sachs *et al.* 2010) and North America (for example, see Bubier *et al.* 1993; or Bellisario *et al.* 1999). However, the relationship between fluxes from heather sites and depth to water table in the current study was positive, i.e. when the water table was deeper, net CH_4 fluxes were higher. This result was unexpected as it is not predicted by existing acrotelm-catotelm models of net CH_4 flux which suggest that a soil profile that contains a greater aerobic proportion will reduce methanogenesis and increase methanotrophy (Clymo and Pearce, 1995; Le Mer and Roger, 2001). Surprisingly, a similar relationship also has been reported in a number of other studies in the UK uplands (McNamara *et al.* 2008; Dinsmore *et al.* 2009a), at other peatland systems in Scandinavia (Kettunen *et al.* 1996; Nykanen *et al.* 1998), Siberian tundra (Sachs *et al.* 2010), and North American bogs (Bellisario *et al.* 1999) and fens (Strack *et al.* 2004; Treat *et al.* 2007). In addition, similar relationships have been found at restored peatland sites (Marinier *et al.* 2004) and during a lab-based manipulation of samples, Moore and Roulet (1993) found that fluxes initially increased during 10 days of water table lowering. Perhaps because observed relationships are weak or because this unexpected relationship between water table and CH_4 fluxes departs from such a strong paradigm, it is often not fully acknowledged or discussed, even when apparent from published data. For example, Dinsmore *et al.* (2009a) disregarded this aspect of their multiple regression which contributed to a high r^2 of 0.80 but contended that maximum CH_4 emissions were associated with water table being closest to the surface because this 'often occured'. The weak positive association between water table and CH_4 fluxes (r^2 = 0.08) observed by McNamara *et al.* (2008) when analysing weekly measurements was not discussed, rather an association between wet locations and high CH_4 emissions was identified (their Fig. 1 and Fig. 4) when comparing fluxes from a variety of locations. Similarly, Bellisario *et al.* (1999) only discussed the expected relationship between water table and CH_4 flux which was apparent when 'a wide range of peatlands' were considered, and not the positive association between water table and CH_4 flux that was identified (r^2 of 0.22). One explanation for the unexpected but frequently observed relationship between water table and CH_4 fluxes at the heather sites is provided by Strack *et al.* (2004) and Sachs *et al.* (2010) who suggest that when water levels are above the surface they either act as a restriction on substrate supply, due to lower productivity, to the system or as a barrier to some of the pathways of CH_4 emission from soils. Alternatively, several studies (Nykanen *et al.* 1998; Marinier *et al.* 2004; Treat *et al.* 2007) identified an increasing depth to water table to be responsible for increased CH_4 emissions. The water table observed by Marinier *et al.* (2004), which was more than 25 cm below the surface for roughly half their sampling period, and the 'disturbed nature' of the field site were suggested for their observation of the unexpected relationship between CH_4 fluxes and water table. Treat *et al.* (2007) and Nykanen *et al.* (1998) suggested that a deepening water table may cause a release of previously stored CH_4. The heather sites in the current study had relatively shallow depths to water table but very rarely moved above the soil surface at any site (Fig. 3.3 to Fig. 3.6) so these hypotheses are not well supported by the current study.

An alternative hypothesis is provided by Kettunen *et al.* (1996) who, after analysing CH_4 fluxes from a Finnish minerotrophic fen and environmental conditions over 14 days prior to the day of flux measurement, were able to identify the hysteresis of CH_4 flux following changes in water table which they suggested may be because 'a rise in water table is followed by a lowering of the water table'. The results of this study show that, in contrast to regression models which used concurrent water table measurements, all multiple regression models with significant running averages of water table always displayed a negative relationship (Fig. 3.20 to Fig. 3.24): when the water table was closer to the soil surface, net CH_4 fluxes were higher. As running averages represented conditions prior to the day of flux measurement, this study supports the suggestion that the response of CH_4 fluxes to water table is delayed. Further evidence for the hysteresis of CH_4 fluxes in response to water table at Lake Vyrnwy comes from a parallel fully replicated manipulation of peat monoliths extracted from the same site (Lukac *et al.* personal communication) which showed a clear delayed response of CH_4 fluxes four months after lowering the water table.

The potential impact of using concurrent measurements of controlling variables to model an output from a hysteretic system is shown in Fig. 3.27. If a CH_4 flux displays an immediate

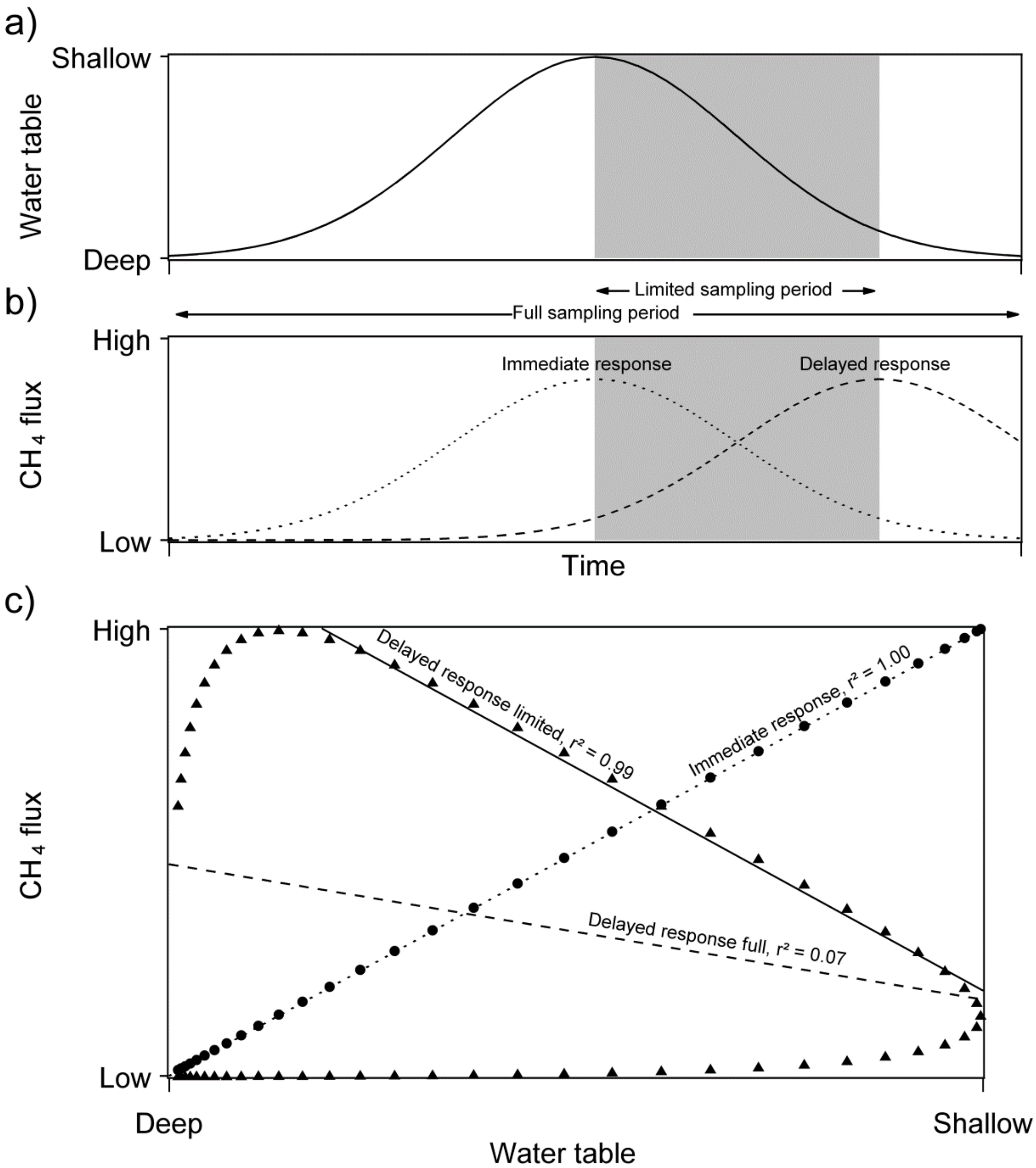

Fig. 3.27 A generalised relationship between CH_4 flux and water and the influence of hysteresis and limited sampling period on regression analysis. The response of CH_4 flux (b) to changing water table (a) can be immediate (········) or delayed (- - - - -). The comparison of CH_4 flux and water table (c) shows that an immediate response (●) produces a strong expected relationship (·········· , r^2 = 1.00) between water table and CH_4 flux, whereas a delayed response (▲) produces either a weak relationship when the full sampling period is used (- - - - -, r^2 = 0.07), or a strong inverse relationship when the sampling period is limited (—— , r^2 = 0.99).

response to a changing water table (Fig. 3.27b), an idealised regression model between these variables would clearly produce an expected strong relationship (see 'Immediate response, $r^2 = 1.00$' in Fig. 3.27c), i.e. when the water table is near to the surface, CH_4 fluxes are high. Without changing the underlying magnitude or direction of the response, the inclusion of a delayed response of the CH_4 flux to water table drastically alters this apparent relationship. A further regression model shows the resulting relationship can become very weak (see 'Delayed response full, $r^2 = 0.07$' in Fig. 3.27c) or, if the sampling period is limited, can become a strong negative relationship (see 'Delayed response limited, $r^2 =0.99$' in Fig. 3.27c) which is actually the reverse of the real effect of water table. The hysteresis displayed in this model may explain the unexpected significant relationships between CH_4 flux and water table seen in a number of studies, particularly those where sampling was temporally limited (Bellisario *et al.* 1999; Marinier *et al.* 2004; McNamara *et al.* 2008; Sachs *et al.* 2010).

3.4.3 Impact of environmental conditions prior to day of flux measurement

As indicated from the results of regression models using running averages of temperature and radiation (Fig. 3.17), there appeared to be a strong hysteresis effect between CH_4 fluxes and changing temperature and radiation. The progression 'in to' and 'out of' phase, as the running average period was extended prior to the day of flux measurement, showed that preceding environmental conditions apparently exerted greater control on CH_4 fluxes than concurrent conditions. Of the studies which identified the influence of preceding conditions on CH_4 fluxes (for example, see Moore and Roulet, 1993; or Kettunen *et al.* 1996) many found a delayed response of CH_4 fluxes to changes in water table which ranged from 7 days (Jerman *et al.* 2009) to 4 months (Lukac *et al.* personal communication). The only published field-based study that identifies hysteresis of CH_4 fluxes in response to temperature appears to be from Song *et al.* (2003) who note a delayed response of around one month, but they did not comment on the significance of soil temperature in controlling the flux. Additional evidence that hysteresis of CH_4 fluxes in response to changing temperature was provided by Updegraff *et al.* (1998) who assessed the influence of thermal history on CH_4 fluxes. Their short-term incubations of peat samples collected from a variety of wetlands showed clear hysteresis and also suggested that the strength of hysteresis of CH_4 emission varied according to availability of substrate. Combined with the generally weak relationship between CH_4 fluxes and environmental variables seen at heather sites in the current study, this may explain why no hysteresis is seen at sites dominated by slow growing vegetation (Smith and Forrest, 1978; Wallen, 1987) .

The combination of running average measurements from soil temperature, solar radiation and water table in multiple regression models revealed complex patterns of control of CH_4 fluxes for Juncus and sedge sites. Hysteresis of CH_4 fluxes from Juncus and sedge dominated sites was evident in response to changing environmental conditions over both short and long time scales. The timing of the response varied for each vegetation type; sites dominated by Juncus responded to changes over a 60 day period prior to measurement for solar radiation and 180 days previously for soil temperature and water table (see Fig. 3.22), but sites dominated by sedge responded to changes that occurred immediately prior (soil temperature and solar radiation) and around 60 days previously (water table, see Fig. 3.23). The existence of two periods of control on CH_4 fluxes is directly supported by a study which manipulated levels of radiation and water table experienced by mesocosms extracted from bog and fen sites in North America (Updegraff *et al.* 2001). Short term CH_4 flux had a strong significant relationship (r^2 between 0.54 and 0.65) with short term productivity of the mesocosms, which was not evident in longer-term comparisons. These authors suggested that root exudates controlled CH_4 fluxes over a short time scale but this relationship was reduced at longer time scales because of the influence of other plant litter inputs.

The hysteresis of CH_4 fluxes to changes in environmental conditions can be explained by a variety of hypotheses which, as they are not mutually exclusive, may combine to produce multiple hysteresis effects, as seen in the current study. Hypotheses include (i) delayed substrate provision, either due to the importance of root death in providing substrate for CH_4 production (Updegraff *et al.* 2001) or due to population dynamics of separate populations which are responsible for each processes leading to the terminal step of CH_4 emission or oxidation (Jerman *et al.* 2009); (ii) acclimation to conditions by the methanotroph or methanogen populations (Blodau and Moore, 2003a); and (iii) storage of CH_4 in soil which delays the exchange with the atmosphere (Moore and Dalva, 1993; Strack and Waddington, 2008). The hypotheses which best explain the hysteresis seen in the current study must account for the differing periods of hysteresis seen at sites with different vegetation. This suggests an abiotic factor such as an extended mean residence time of CH_4 in soil is less likely, but that temporal variation in substrate provision from different plant communities may result in different levels of carbon input (Smith and Forrest, 1978; Wallen, 1987) and different speeds of decomposition of plant litter seen in similar blanket bogs (Heal *et al.* 1978; Latter *et al.* 1998). Alternatively, differences in functional genes for methanogenesis and methanotrophy which were significantly associated with net CH_4 flux at the Lake Vyrnwy site (Freitag *et al.* 2010) showed that differences in microbial activity occurred at small spatial scales which may affect the ability of the methanotroph and methangen population to acclimatise to changing conditions.

3.4.4 Sampling strategy and the analysis of environmental controls on CH_4 fluxes

The sampling of CH_4 fluxes in this study incorporated seasonal variation across 14 months, and spatial variation which was stratified by vegetation type. The range of variation in CH_4 fluxes explained by environmental variables in this regression analysis (11.8% to 49.3%, see Table 3.2) are at the lower half of values from similar studies at other peatland sites (for example, see Saarnio *et al.* 1997; or Dinsmore *et al.* 2009a) which range from 17% (Laine *et al.* 2007) to 98% (Fowler *et al.* 1995a). Of the studies at other sites, those which used measurements taken in a variety of conditions throughout the year appear to produce results with lower r^2. This includes Ward *et al.* (2007) who sampled over 15 months and explained 23.5% to 36.5% of variation in CH_4 fluxes and Laine *et al.* (2007) who sampled over 14 months and produced 21 models for each plot resulting in a wide range of explained variation (17% to 87%). In contrast, studies which have explained higher proportions of variation tend to be those which were limited to a period of one month or less (such as Fowler *et al.* 1995a who explained 98% of variation), or those which combine all temporal variation of fluxes to a single seasonal value (such as Bubier *et al.* 2005 who explained 60% to 94%). The delayed response to environmental conditions observed in the current study provides one suggestion as to why analyses of data sets with greater temporal variation explain a limited proportion of variation. Specifically, as all stages of a seasonal cycle are included in the analysis, hysteresis of CH_4 fluxes in response to environmental conditions caused the relationship between CH_4 fluxes and concurrent environmental conditions to deteriorate. To test the influence of using limited temporal variation, a further regression analysis was undertaken following the same methods as the multiple regressions between CH_4 fluxes and concurrent environmental variables (see Section 3.2.3.1). Single seasonal averages for 2009 of CH_4 flux and environmental conditions were used as model inputs in order to remove all temporal variations. There were no significant relationships between CH_4 fluxes and any environmental variables for fluxes from grass sites, but very high proportions (>99%) of variation in fluxes from heather, Juncus and sedge sites were explained by air temperature, rainfall and humidity, respectively. These results suggest that most unexplained variation in CH_4 fluxes at Vyrnwy was due to temporal, rather than spatial variation.

3.4.5 Impact of ditch blocking on CH_4 flux

The blocking of drains has been shown to produce a gradual recovery of hydrological conditions of the blanket bog at Lake Vyrnwy. For example, depth to water table was reduced ca. 2 cm downslope of blocked drains and, unlike unblocked locations, depth to water table responded strongly to rainfall in blocked sub-catchments (Wilson *et al.* 2010). As water table is a commonly identified controller of net CH_4 flux from a variety of wetlands (Bubier *et al.* 1993, inter alia) this change in management practice can also be expected to influence the balance between CH_4 production and oxidation as the size of the anoxic and oxic zones of the soil column is altered (see Le Mer and Roger, 2001).

As well as accounting for other putative controls of CH_4 flux, the spatial stratification of a landscape has been shown to dramatically improve landscape estimates of CH_4 flux by Schrier-Uijl *et al.* (2010) who used chambers with a measurement area of 0.072 m^2 to estimate the CH_4 flux from an area within the footprint of an Eddy Covariance (EC) system. Without stratification, the estimate from the chamber measurements was more than 55% lower than the EC-derived estimate (which was assumed to be an accurate integrated measurement from the entire area), whereas with stratification there was only a 13% difference between the methods. Stratification, however, does not always result in comparable results from different scales of measurement as shown by Teh *et al.* (2011)whose discrepancies between EC and chamber measurement were due to the heterogeneous landscape in which measurements were made. Despite stratifying measurements by vegetation and elevation there was still no measured significant effect of drain blocking on CH_4 fluxes at Lake Vyrnwy.

Placing this result in the context of published studies is not straight-forward; whilst direct manipulations of the water table in extracted samples have been relatively common and shown to significantly affect CH_4 fluxes (e.g. Daulat and Clymo, 1998; Urbanova *et al.*

2011), the number of *in situ* comparisons between drainage treatments in wetlands is limited. Furthermore, results from tests of the effect of wetland drainage or restoration are not always clear as the low number of replicates in field manipulations often prevents any statistical comparison between treatments (e.g. Hughes *et al.* 1999; Fenner *et al.* 2011). In addition, pseudoreplication of sampling (*sensu* Hurlbert, 1984) may only show significant differences between sites, rather than clearly identify the effect of any treatment (e.g. Nykanen *et al.* 1995; Strack and Waddington, 2007). Nykanen *et al.* (1998) compared a total of 25 drained and natural wetlands in Finland and found a strong effect of drainage on CH_4 fluxes ($p<0.001$) in nutrient poor sites (ombrogenous bogs). However, the drained sites had also been used for forestry for between 30 and 50 years so it is not clear whether differences in CH_4 fluxes were only a result of hydrological changes or due to other observed changes including soil structure, pH, air temperature, microform and vegetation. Whilst the study at Lake Vyrnwy was made within a balanced, independent, manipulated design at a landscape scale, there was no apparent response of CH_4 flux to the blocking of drains. Given the strong response of CH_4 flux to water table manipulations in mesocosm experiments (Daulat and Clymo, 1998 *inter alia*), the absence of response was unexpected. This may be attributed to several reasons: (i) high spatial variability in the response of hydrological conditions to drain blocking; (ii) the length of time which a landscape responds to a change in hydrological regime; (iii) a lack of statistical power of the current study, which only had three replicates; (iv) the absence of response to the initial changes in hydrological regime when drains were first constructed at the site; and/or (v) underlying geomorpholigical status of the site which means water table is robust to drain blocking. Wilson *et al.* (2010) and Kelly (2008) observed significant changes in water table depth in blocked sub-catchments at Lake Vyrnwy within the same timescale as the current study but sampling in both of those studies was concentrated around drains. In contrast, sampling in this study was arbitrarily made within each combination of factors (elevation, vegetation and drainage treatment) but not focused specifically around drains. As no significant difference in water table measurements between blocked and unblocked was observed (after controlling for vegetation and elevation; Friedman's ANOVA, $p = 0.274$), a heterogeneous spatial response of hydrological conditions to drain blocking is one possible contributing factor. Further landscape scale manipulations which include more replicates, or further stratification of sampling to account for spatial heterogeneity within each replicate, would better reveal the response of CH_4 flux to drain blocking.

3.4.6 Summary

Soil temperature and water table were the environmental variables which were most consistently associated with CH_4 fluxes, however, the relationship between fluxes and water table did not always control CH_4 fluxes in an expected manner. At some sites CH_4 emissions were lower when the water table was closer to the surface, a result which contradicted the acrotelm-catotelm model of CH_4 flux, but may be explained by the hysteresis of fluxes in response to changing water table. Strong hysteresis of CH_4 fluxes was also apparent in response to temperature and radiation. A replicated landscape-scale experiment of water table manipulation was expected to cause changes in CH_4 flux but, despite controlling for other aspects of spatial variation, no significant effect on CH_4 fluxes was observed.

Chapter 4 The effect of temporal and spatial biases of measurement methods on apparent CH_4 flux

4.1 Introduction

Blanket bogs in the UK Uplands are heterogeneous landscapes due to a combination of natural and anthropogenic factors. For example, spatial variation in vegetation (see Section 2.3.2 and Fig. 2.7), hydrology (Wilson *et al.* 2010 who examined the effect of different hydrological management practices), and climate (see Section 3.3.1) at the blanket bog around Lake Vyrnwy occur at a variety of different scales. One specific example is the high level of microclimate variation reported by Suggitt *et al.* (2011).

In addition to this marked spatial variation, temporal variations in environmental conditions such as temperature, PAR and depth to water table also occurs, with both diurnal and annual cycles (Fig. 3.3 to Fig. 3.15). CH_4 flux has been observed to be controlled by some of these dynamic features at Lake Vyrnwy with depth to water table and soil temperature being the most consistent (see Section 3.3.2). Other studies report similar and additional control by all of these features at other wetland sites such as vegetation (Dinsmore *et al.* 2009a), hydrology (Bubier *et al.* 2005), air temperature, soil temperature and PAR (Ward *et al.* 2007). The heterogeneous nature of these controllers of CH_4 flux contributes to the complex and varied patterns of CH_4 fluxes observed in many *in situ* wetland studies *(inter alia* Waddington and Roulet, 1996).

In addition to the inherent variability in CH_4 fluxes, additional variation in estimates can be expected as a result of biases in sampling methods. The commonly used method of manual chamber is always limited to the times at which field sites are visited. In some cases this means temporal series of measurements are always made at the same time of day (Fenner *et al.* 2011), but in most studies measurements are limited to daylight hours only (Section 2.2.2, e.g. Alm *et al.* 1999). If a CH_4 flux displays no temporal variation, then time restricted measurements would still be representative of longer time periods. Conversely, consistent diurnal cycles of CH_4 fluxes combined with biased sampling towards a particular time of day could lead to important systematic measurement bias.

Diurnal variations of CH_4 flux from wetlands may occur for several reasons. Direct factors include the control of rates of methanogenesis, and to a lesser extent rates of methanotrophy (King and Adamsen, 1992), as a result of diurnal variations in soil temperature, which themselves may display a delayed response to diurnal patterns of air temperature (see Fig. 5 in Laine *et al.* 2007). Indirect factors may include any diurnal variations in the temporal functions of plants as providers of substrate for methanogenesis, and/or as pathways for the transport of CH_4 from the sub-soil to the atmosphere through aerenchymous tissue. Substrate provision by plants, whether via carbohydrates used for acetotrophy or CO_2 used for CO_2 reduction, is an important control of CH_4 flux (Le Mer and Roger, 2001). The association between substrate supply and microbial methanogenesis is well established (Whiting and Chanton, 1993), yet the understanding of the speed of response of CH_4 fluxes to newly introduced carbon substrate is less clear. For example, King *et al*. (2002) observed that atmospheric CO_2 was assimilated by wetland plants, discharged as a substrate for methanogenesis to microbial populations in the soil, and re-emitted back to the atmosphere as CH_4 within two hours. This is in marked contrast to a study by Joabsson *et al.* (1999) who didn't see any significant reduction in CH_4 flux until after 34 days of shading treatment to the above ground vegetation. The function of aerenchymous tissue as a CH_4 conduit is complicated as, dependent on the wetland plant species involved, two processes may be occurring (Section 4.1.4 in Lambers *et al.* 1998). The first, diffusion, is a result of the CH_4 concentration gradient between the soil and atmosphere and does not vary greatly with diurnal changes in temperature (Chanton, 2005). In contrast, the second, an active gas flow system, is produced by internal pressure gradients, or humidity differentials, and is a result of diurnal cycles of insolation (Chanton *et al.* 1993).

As a result of the combined influence of all these factors, diurnal measurements of CH_4 flux at different peatland sites have produced diverse results. For example, studies have either shown the absence of diurnal variation (Greenup *et al.* 2000) or CH_4 fluxes which peak during hours of daylight (Fowler *et al.* 1995b) or darkness (Laine *et al.* 2007). At our current state of knowledge, without direct measurements, the diurnal patterns of CH_4 flux at a particular study site cannot be predicted, and any estimation of resulting measurement bias, is not possible.

In addition to the method of chamber deployment, chamber designs are equally important in generating possible systematic measurement biases and have been studied extensively. For example, by creating a controlled spatially homogeneous efflux of CO_2 through an artificial mineral soil (of quartz sand), Pumpanen *et al.* (2004) were able to compare fluxes from a variety of chamber designs against a known reference flux. They were able to examine a number of features of chamber design, including the influence of internal fans, vents, collars, air flow-through and saturation of the headspace during measurements. One feature of chamber design that was not examined, and is rarely examined in other published studies, is the effect of enclosing different sized areas or "footprints" within a chamber. As for temporal variation, if a CH_4 flux displays no spatial variation, then spatially limited measurements such as those made with a small chamber, would be representative of larger areas. However, in reality CH_4 fluxes are highly spatially variable and, as a result, a limited chamber size may lead to systematic measurement bias depending on the inherent scale (or "grain" *sensu* Dungan *et al.* 2002) of any spatial heterogeneity. Specifically, as a balance of the microbial production and oxidation of CH_4, net CH_4 fluxes ultimately occur at a microbial scale (Le Mer and Roger, 2001). Net CH_4 fluxes are also influenced by proximal processes, such as the aerenchymous transport of CH_4 from the catotelm (Clymo and Pearce, 1995) to the atmosphere, which also vary at small scales. For example, artificial conduits which replicated the role of aerenchymous tissue as a pathway for CH_4 efflux, were found to be just 1 mm in diameter (Greenup *et al.* 2000). Even the smallest sized sampling methods, such as the 10 cm diameter chambers used by Hughes *et al.* (1999), integrate all this small-scale variation into a single CH_4 flux measurement.

An untested assumption of making multiple flux measurements in a spatially heterogeneous landscape is that the use of chambers which enclose smaller areas will produce estimates with larger variances (Davidson *et al.* 2002; Denmead, 2008). However, comparisons between methods which measure fluxes from different sized areas are typically also made using different methodologies and, frequently, with different ways of spatially extrapolating the estimates (see Prieme *et al.* 1996; Riutta *et al.* 2007). This means the direct impact on flux estimates of “footprint size” is rarely directly examined. Potential effects of “footprint size” include the ratio of chamber edge to chamber area. For example, a relatively large chamber edge may affect the relative bias of soil disturbance, including root severance (Heinemeyer *et al.* 2011), and leakage of headspace concentration (Tingey *et al.* 2000). The method followed by Czobel *et al.* (2005), who used a series of chambers enclosing different sized areas (between 0.004 and 4.5 m^2), did enable an assessment of chamber area, but they did not directly test for the effect of area. However, their results indicate that the smallest chambers not only had the highest variation, but also the largest net uptake of CO_2. Whilst conforming to predictions that spatially heterogeneous fluxes combined with small chambers will increase variability, it is not clear how smaller chambers may result in increased photosynthesis, but respiration may be reduced as a result of root severance (Heinemeyer *et al.* 2011). Although some work has been carried out on CO_2 fluxes, any such effect on CH_4 fluxes are yet to be identified. The inherent variability and the spatial and temporal limitations of sampling methods contribute to the high variability of CH_4 flux estimates, such as the coefficient of variation of between 30 - 100% found by Prieme *et al.* (1996). One consequence of such high variability may be the difficulty in adequately identifying the controls of CH_4 fluxes. For example, a regression model between CH_4 fluxes and environmental variables constructed for a site in Finland (Saarnio *et al.* 1997) did not significantly explained CH_4 fluxes measured at the same site several years later (Becker *et al.* 2008).

In the study presented here, a series of experiments examined specific questions relating to the temporal and spatial variability of CH_4 fluxes at the blanket bog around Lake Vyrnwy. Specifically, in order to identify any diurnal cycle and any resulting bias in the measurements limited to daylight hours in Chapters 2 and 3, the hypothesis that CH_4 fluxes significantly differed between day and night was tested for areas dominated by different vegetation types and during different times of the year. In addition, in order to assess the effect of using chambers of limited sizes in a heterogeneous landscape, the hypothesis that apparent CH_4 flux was significantly altered by the size of chamber used to measure was also tested.

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4.2 Materials and methods

4.2.1 Comparison of diurnal CH_4 fluxes using continuous measurement system

4.2.1.1 Study site description

All measurements were made at a single site in the upland blanket bog around Lake Vyrnwy, North Wales (see Section 2.2.1), and located 40 m from the Hirddu meteorological station on a ridge to the south of the Hirddu Fawr stream (Fig. 2.1). The site included discrete patches of vegetation, each dominated by grass, heather, Juncus or sedge (see Section 2.1 for details) and was the location for flux measurements during two measurement campaigns: the first was during May 2010 and the second from the end of August to the start of September 2010. Two weeks prior to the start of the first set of measurements, three collars, 20 cm in height, were inserted ca. 5 cm into the soil (precise values were recorded for the calculation for headspace volume) of each vegetation type and used for the subsequent measurements during both campaigns.

4.2.1.2 Flux measurements

Near-continuous measurement of CH_4 fluxes was achieved by combining a cavity-enhanced-absorption spectrometer (Fast Greenhouse Gas Analyzer (FGGA), model 907-0010, Los Gatos Research, Inc., Mountain View, CA, USA, see Mastepanov *et al.* 2008 for example) together with an established multiplexed automatic chamber system (Heinemeyer *et al.* 2007). Specifically, the FGGA was connected in parallel to an automated system which used an infra-red gas analyser (IRGA, model 8100, Li-Cor, Lincoln, NE, USA), 12 long term chambers (model 8100-101, Li-Cor) and a custom-built multiplexing unit (Biology Electronic Services, Biology Department, University of York, UK) which facilitated automatic hourly flux measurements using both gas analysers (CH_4 and CO_2) from each chamber. Each flux measurement consisted of a period of 180 s, during which the chamber was automatically sealed and changes in headspace concentration over time were used to calculate the apparent flux.

Previous measurements made with this custom-built multiplex unit and other similar systems have been restricted to sites either without vegetation (including forests without understory vegetation) or where vegetation is not taller than ca. 15 cm (see Heinemeyer *et al.* 2011 for examples from several different ecosystems). In order to remove this constraint and enable flux measurements to be made on sites that include taller vegetation, such as ericaceous dwarf shrubs, the modifications described below were made to nine long term chambers by Biology Electronic Services and Biology Mechanical Workshop Services (Biology Department, University of York, UK).

The modified automatic chambers were based around Li-Cor long-term chambers and maintained several design features, including: (i) multiplexed system capable of automatically measuring up to 16 collars; (ii) software to control the order, frequency and duration of measurements; (iii) mechanism to open the chamber top (dome) to minimise disturbance to the soil and vegetation within each collar when the chamber was open. Modifications were required to enclose taller vegetation resulting in the raising of the original dome ca. 50 cm above the soil surface, and taller vertical sides, that retracted downwards when the chamber was open, to entirely enclose the headspace.

Schematic diagrams of the chamber design and *in-situ* photo are shown in Fig. 4.1. The transparent dome and opaque mechanism (arm) for opening and closing the dome were retained from the original chambers but an upper Perspex plate, 12 mm, was added, onto which the dome of the chamber sealed when closed. The upper Perspex plate was positioned 47.5 cm above a lower opaque base plate which sealed over the 20 cm diameter soil collar with a rubber flange (Fig. 4.1). The lower plate did not rest directly on the soil surface; rather the entire chamber was supported with thin adjustable aluminium legs.

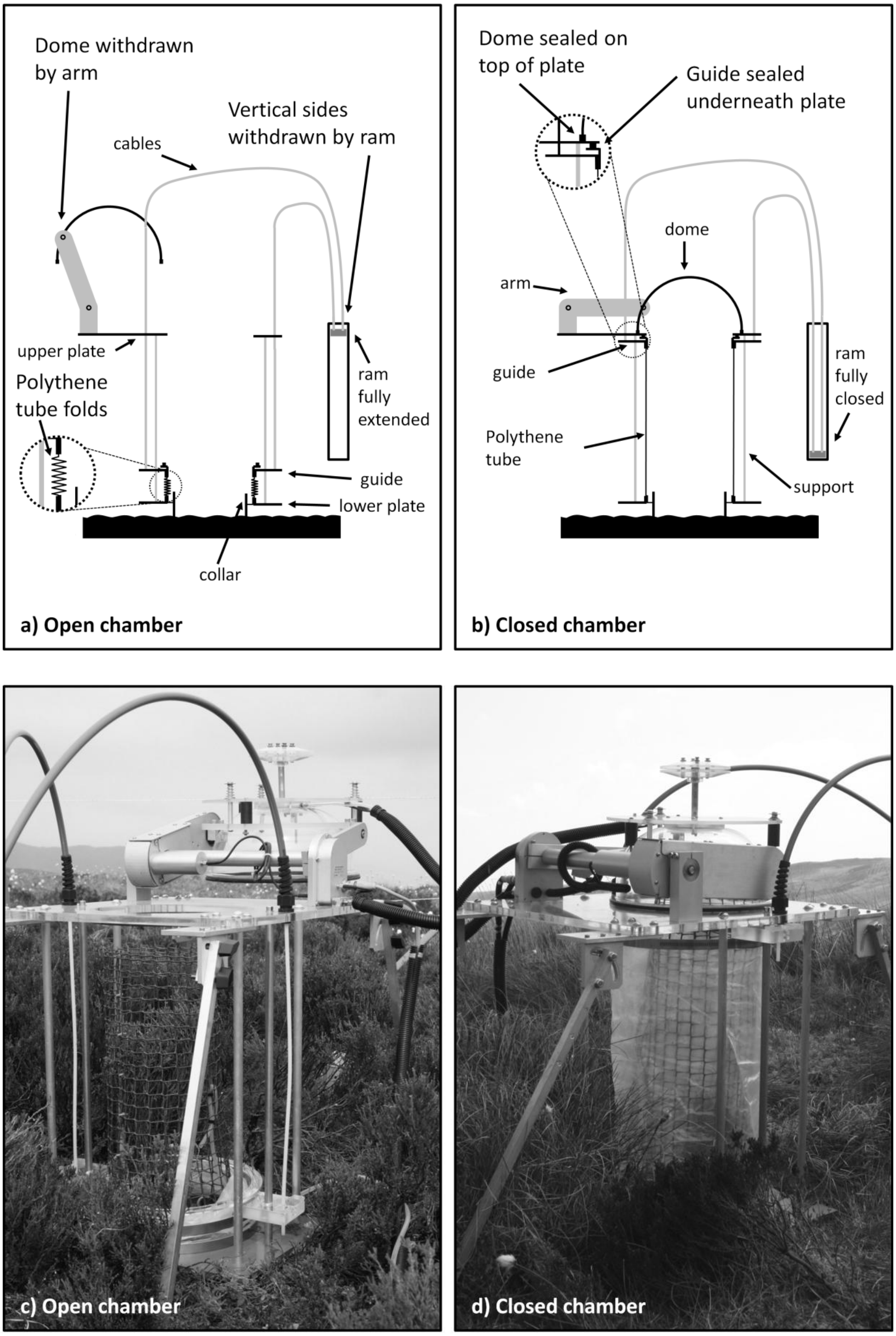

Fig. 4.1 Schematic diagram and photos of the modified Li-Cor long term chamber which, in addition to a moving dome, had a "concertina" sleeve that folded downwards when open (a;c) and was pulled upwards with a ram in order to fully close the chamber (b;d).

In order to enclose the chamber headspace, a 25 cm diameter flexible “concertina” sleeve made of UVI polythene sheeting (product code PM0027, First Tunnels Ltd, Barrowford, Lancs., UK) was attached to a protruding lip on the lower plate by a jubilee clip compressed onto a 1 cm wide rubber pad. The flexible sleeve was attached to a transparent movable circular guide which was raised or lowered as the chamber was closed or opened. The vertical movement of the guide was achieved by two cast acrylic rods (5 mm diameter, The Plastic Shop, Coventry, UK) which were both attached to a separate ram (18 inch actuator, Maplin Electronics, Rotherham, UK) and synchronised with the movement of the dome. Once raised, the top of the guide was pulled against a circular gasket on the underside of the upper plate with the effect that the polythene sleeve became the vertical sides of the closed and chamber and was effectively sealed at both ends. Vegetation was contained within the chamber, and prevented from either damaging, or being damaged by, the moving polythene sleeve, by an inner sleeve of plastic-coated wire netting.

Whilst being able to enclose vegetation up to ca. 60 cm above the soil surface, the tall chambers were designed to mimic the original (short) chambers ability to minimise disturbance to the soil and vegetation within each collar when the chamber was open. Specifically, the potential bias from shading, the increase in temperature and the sheltering of soil and vegetation from rainfall and wind was minimised by the lowering of the vertical sides of the chamber cylinder, which did not extend more than 5 cm above the collar when open. The polythene concertina provided suitable flexibility for the chamber sleeve and, in order to prevent distortion of the chamber volume during measurement, was extended so that it did not move in windy conditions. In addition, the main upper components of the tall chamber where made from Perspex to minimise shading and each chamber was positioned so that when open, its dome and moving arm where to the North of each collar.

4.2.1.2.1 Comparison of modified and unmodified chambers

Modified tall chambers were used to measure fluxes from sites with heather, Juncus and sedge vegetation and unmodified short chambers were used on sites with shorter grass vegetation. Given the increased volume of the tall chambers relative to the measured surface, and despite the increased headspace mixing by the spatial distribution of inlet and outlet pipes, it is possible that a systematic error in fluxes measured with tall chambers was created due to vertical differences in trace gas concentration: a problem which is commonly solved with the addition of internal fans (see Davidson *et al.* 2002 for a discussion of the effect of adding fans). Laboratory-based comparisons between both types of chambers were made to empirically determine if the different chamber design led to differences in observed fluxes of CH_4 or CO_2. Additionally, tests were made to establish the need for an internal fan within the tall chambers. The short Li-Cor chambers are not produced with internal fans but use the constant flow-through of air, provided by the inlet and outlet pipes leading from and to the gas analyzer, to enhance headspace mixing (Davidson *et al.* 2002). Adjustments were made to the tall chamber so that the inlet pipe was positioned ca. 20 cm from the soil surface but the outlet pipe was positioned at the top of the dome of the chamber, in contrast to the short chamber where both inlet and outlet pipes were positioned at the top of the dome.

4.2.1.2.2 Comparison of modified and unmodified chambers - methods

A soil, known to strongly oxidise CH_4 (Wang and Ineson, 2003), was obtained from Grimston Wood, near York. To maximise and standardise the observed fluxes, samples from the O horizon (specifically the F and H layers) were taken and passed through a 5.6 mm sieve to remove all roots. The soil was well-mixed and 2.5 l placed into each of eight collars, 20 cm in diameter and 10 cm in height, which had been sealed to an underlying MDF board.

All eight collars were measured with the short and tall chambers within a 90 minute period using the multiplexed system described above. Half of the samples were measured first with tall chambers and then with short chambers, and the other half of samples were measured in an alternative order, with random assignment of each sample into either group. Specifically, after a pre-experiment measurement, all samples were ranked and placed in pairs of similar initial CH_4 flux. Then each sample from any pair was randomly allocated into one of the two different measurement groups.

A similar experimental design was followed for testing the inclusion of internal fans within the tall chambers. Using the allocation procedure as above, the eight same soil samples were measured once with tall chambers, either with or without an internal fan. When included, a 0.84 W brushless fan motor (model 2408NL-04W-B10, NMB (U.K.) Ltd, Bracknell, UK.) was placed approximately half up the tall chamber (ca. 25 cm from the soil surface) and positioned so that air flowed in an upwardly direction whilst the chamber was closed. Fluxes were calculated for both experiments with the same algorithm described for the study comparing diurnal CH_4 fluxes (see Section 4.2.1.3) and appropriate paired comparisons made, firstly, for the tests of chamber type and, secondly, for the effect of adding fans.

4.2.1.2.3 Comparison of modified and unmodified chambers - results and discussion

There was no significant difference between observed fluxes of CH_4 (Wilcoxon signed-rank test, $p = 0.055$) or CO_2 ($p = 0.148$) when tall and short chambers were used. Whilst the p-value for CH_4 was close to significance, the median observed rate of methane oxidation was highest in the tall chambers; an unexpected result had the volume of the tall chamber made it harder to detect changes in the headspace concentration. In addition, there was no significant difference between observed fluxes of CH_4 (Wilcoxon rank-sum test, $p = 0.248$) or CO_2 ($p = 1.000$) when fans were either present or absent during chamber closure. These empirical tests on the tall chambers suggested they functioned in an equivalent way to the unmodified short Li-Cor chambers and that any reduced mixing in the larger headspace of the tall chambers did not significantly alter measured fluxes.

4.2.1.3 Data handling

CH_4 fluxes were calculated using the slope of linear regression between headspace concentration and time during each chamber closure. Within the 180 second period that each chamber was monitored, an initial 'dead band' (Li-Cor Biosciences, 2007) of up to 90 seconds was identified, after which time the vertical sides and dome of the chamber had fully moved into a closed position. Changes in the measured headspace concentration during this dead band were discarded to negate any influence on the regression slope of each flux measurement.

A decision algorithm was used to assess fluxes produced from the regression slope whereby all slopes which were significantly different from zero (at the $p < 0.05$ level) were accepted for further analysis. Of the flux measurements which were not significantly different from zero, any with a coefficient of variation (CV) of the headspace concentration equal to or greater than 0.5 % were discarded as they were considered to be non-linear. Alternatively, any with a CV of less than 0.5 % were accepted and counted as zero fluxes, as they showed no net exchange of CH_4.

A final component of the algorithm identified any unusual patterns within a chamber closure by comparing fluxes during the first and last 45 seconds of each measurement period. If the absolute value of any of these fluxes differed by more than 0.5 mg CH_4 m^{-2} h^{-1} then the flux measurement was manually reviewed and a decision made either to accept the initial decision or discard the flux. Out of a total of 1234 flux measurements, 75 were manually reviewed and 26 were discarded. In addition to producing consistent, objective results this algorithm also matched previous experience in screening for unusual flux measurements. Such discarded measurements occurred for a variety of reasons, including trapped vegetation, trapped cables, or faults with the rams.

Fluxes (mg CH_4 m^{-2} h^{-1}) were calculated from the changes in headspace concentration (ppm) over time as in Equation (2.1), including an adjustment for air temperature, headspace volume and area of soil within the chamber. Missing fluxes, due to removal by the decision algorithm, were not gap filled.

Separate analyses were made for each campaign (May and August 2010) to assess diurnal differences in fluxes. Measurements of solar radiation from the adjacent meteorological station were used to distinguish whether fluxes were measured in daylight or darkness. Due to the difference in diurnal length and occasional gaps in the flux measurements from each chamber (due to system failure or removal by the decision algorithm), four measurements from each diurnal period were randomly selected and summed to produce single day and night values from each chamber for each campaign. The differences between summed day and night values from each chamber were tested for normality (Kolmogorov-Smirnov) and appropriate statistical comparisons were made to test for the effect of diurnal period on CH_4 fluxes. A secondary statistical comparison between CH_4 fluxes from different vegetation types also used the randomly selected fluxes from each chamber (as described above), regardless of diurnal period. Total flux estimates for each chamber were tested for normality and homogeneity of variance (Levene's) before an appropriate test on the effect of vegetation and any *post hoc* analyses.

4.2.1.4 Regression between CH_4 flux and environmental variables

A meteorological station (WS-GP1 and associated sensors, as described in Section 3.2.2, Delta-T Devices, Cambridge, UK) and pressure sensors (Baro-Diver, Sclumberger Water Sevices, Delft, The Netherlands) were established at the site and gave uninterrupted quarter-hour readings of air temperature, soil temperature at a depth of 10 cm for each vegetation type, PAR, solar radiation, humidity, wind speed, wind direction and atmospheric pressure during, and two weeks prior to, each campaign.

Using the same method described in Section 3.2.3, the environmental variables which best explained the variations seen in CH_4 flux measurements from all chambers, and from each vegetation type, were identified using a regression approach. Specifically, forward step-wise multiple regression models were constructed (see Section 3.2.3.1 for further details) for fluxes from each subset of chambers and concurrent environmental variables. Concurrent environmental variables were calculated as the average value over a 15 minute period which was closest to the time of flux measurement or, in the case of rainfall, the total value over the closest 15 minute period.

The suggestion of a delayed response by CH_4 fluxes to changing environmental conditions in Section 3, and the hysteresis effect seen in the short-term response of CH_4 fluxes to temperature (Updegraff *et al.* 1998) and PAR (Joabsson *et al.* 1999) meant a second regression approach was undertaken which used a running average over the period prior to the time of flux measurement (see Section 3.2.3.2 for further details). Individual single regression models were created for CH_4 fluxes from each combination of vegetation type and all periods of running average for each environmental variable, where the running average ranged from 15 minutes to 10 days and increased in 15 minute intervals (see Section 3.2.3.2).

4.2.2 Impact of chamber area on apparent flux

4.2.2.1 Study site description

Measurements were made within 100 m^2 of upland blanket bog in the upland blanket bog around Lake Vyrnwy, North Wales (as generally described in Section 2.2.1), located in the Eunant catchment on a ridge to the south of the Eunant Fach stream (SH 93256 23040, see

Fig. 4.2). Elevation at the site varied between 496 - 524 m.a.s.l. and, whilst the site initially appeared as a single patch of vegetation dominated by heather and sedge, heather coverage actually varied between 5% and 70% within the 7.5 m^2 locations for flux measurements. All measurements were made between the 18th and 25th of August, 2009.

4.2.2.2 Flux measurements and data handling

12 locations were each measured with four static non-steady state chambers of varying sizes. Three of the chambers were constructed from Perspex cylinders, 40 cm in height, sealed to collars, 20 cm in height, which were inserted into the soil. The height of the chambers and collars were uniform, yet their diameter differed between 10 cm, 30 cm and 90 cm which resulted in different areas over which fluxes were measured of 0.00785 m^2, 0.0707 m^2 and 0.636 m^2, respectively. The fourth type of chamber was based on a previously developed agricultural cloche system (for example see the 'mega-chamber' in Pangala *et al.* 2010) whereby semicircular steel hoops (Premier Polytunnels, Barnoldswick, UK) were inserted into the ground to support a cloche cover made from a layer of transparent fabric (Woven Ripstop Film Translucent, Shelter Systems, Santa Cruz, CA) and a layer of polythene sheeting. Five hoops, 1.5 m wide at the base and ca. 0.8 m high, were evenly spaced over 5 m which resulted in a much larger area, 7.5 m^2, of measurement than could be achieved with a portable chamber. The cloche cover extended beyond the hoops to form a flange, ca. 50 cm wide, all around the cloche and a double layer of sandbags was used to seal the flange and make an effectively airtight headspace inside the chamber.

Fluxes were calculated using the slope of linear regression between CH_4 concentration and time for each individual measurement. Changes in headspace concentration and subsequent flux determination were calculated by two methods depending on the type of chamber:

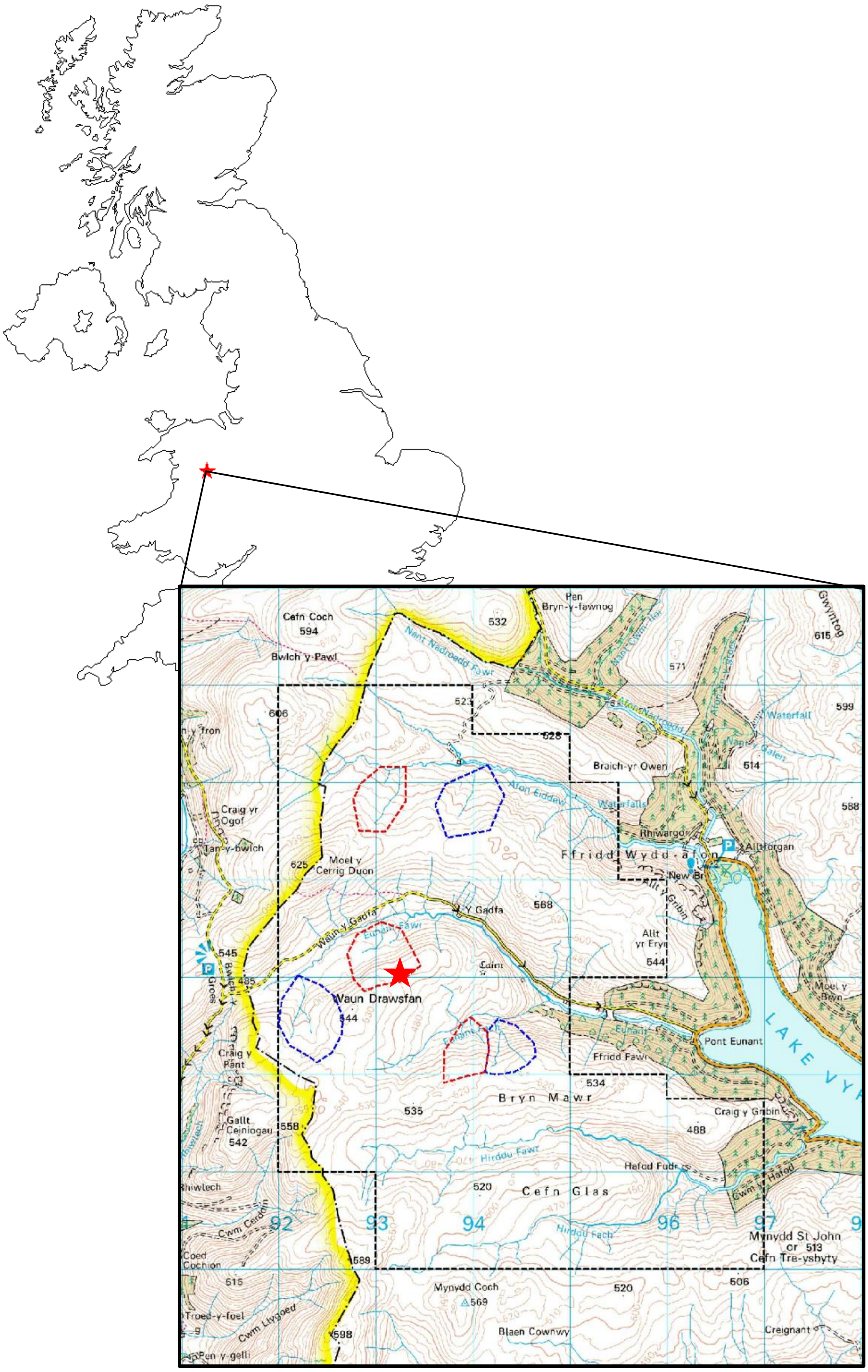

Fig. 4.2 Location of Lake Vyrnwy with the study site for different measurement areas highlighted with a red star (SH 93256 23040).

(i) Cloche. Once the flange of the cloche cover was sealed with sandbags, fluxes inside the cloche were determined with an established method (for example Pangala *et al.* 2010) using an internal open-path Tuneable Diode Laser (TDL, Gas Finder 2.0, Boreal Laser Inc., Edmonton, Canada), which had been set up inside the cloche prior to sealing, to measure changes in CH_4 concentration at a rate of 1 Hz. Measurements were made for a period of 15 minutes, whilst ensuring that significant leakage did not occur (see below). The laser from the TDL was transmitted across the length of the cloche (4 m) to a retro reflector unit and returned in a parallel path where it was received by a detector. Both the TDL and retro reflector were mounted on tripods at a height of ca. 0.6 m.

In order to ascertain rates of leakage from the cloche, N_2O was added to the chamber headspace and used in a similar manner to SF_6 in Section 2.2.2. Whilst N_2O is not a *sensu stricto* inert gas with which to trace leakage, N_2O fluxes were always observed to be below detection (emission or uptake) at several blanket bog sites in Vyrnwy less than 2 km away (Toet, personal communication). As with SF_6, any changes in N_2O headspace concentration observed in the cloche were consequently attributed to leakage rather than soil exchange. The use of N_2O during this study also meant leakage could be monitored in real time and, if appropriate, cloches could be re-sealed before re-attempting a measurement.

Rates of leakage from the cloche were determined by the addition of 70 ml of 100% N_2O to the headspace through 1.5 m of vacuum tubing (1.6 mm internal diameter, Tygon Formulation R-3603 Tubing, Part number AAC00002, Saint-Gobain Performance Plastics, Akron, OH, USA), immediately after the cloche was sealed. An internal fan, positioned next to the end of the vacuum tubing, ran for 30 seconds to assist even distribution within the headspace. Subsequently, the headspace concentration of N_2O was measured using a photo-acoustic infrared analyzer (INNOVA 1412, LumaSense Technologies, Santa Clara, CA, USA) which extracted consecutive samples, 300 ml, with an intermittent pump from the cloche at 2-minute intervals. Samples were extracted through 2 m of PVC tubing (4 mm internal diameter, Portex, Product code 800/000/280, Smiths Medical International, Hythe, UK) which passed from a suspended position ca. 0.5 m from the soil surface in the centre of the cloche, underneath the sealed flange, and to the external analyser.

Each flux was calculated using an algorithm which, in addition to calculating the flux from the slope of linear regression between CH_4 concentration and time, was designed to objectively determine if leakage should be compensated for, or if a flux measurement should be entirely discarded. In a similar manner to the algorithm described in Section 2.2.3, fluxes were accepted if a strong linear relationship ($r^2 \geq 0.9$) existed between CH_4 concentration and time; they were also adjusted for leakage if the decline in N_2O concentration was also linear ($r^2 \geq 0.9$). However, fluxes were also discarded if more than 25% of the maximum headspace concentration of N_2O leaked from the cloche during the measurement period, which indicated significant system leakage.

Once finished, all components of the cloche were quickly removed and within a mean (±standard error of the mean, SEM) of 44 (±4.8) minutes, measurements commenced with the three smaller Perspex chambers inside the same area measured by the cloche.

(ii) Cylindrical Perspex chambers. This method follows a similar method described in Section 2.2.2. Briefly, the collars for each size of cylindrical Perspex chamber were gently inserted into the soil and the seal between collar and soil improved by packing sand around the exterior of each collar. Chambers were then sealed to each collar with reinforced transparent tape and fluxes were determined by the extraction of six consecutive gas samples, 20 cm^3, from each chamber at five minute intervals over a 25 minute period. The exact time of extraction was recorded and, after GC analysis for CH_4 and SF_6, the slope of linear regression between CH_4 concentration and time for each measurement was calculated. SF_6 was added prior to the initial sample extraction in order to estimate rates of chamber leakage but, unlike the method in Section 2.2.2, the chamber headspace was not enhanced with CH_4 as the site was relatively wet and CH_4 oxidation was not expected.

Each flux was calculated using an algorithm which was designed to objectively remove any erroneous data time points from a single series and to determine if leakage should be compensated for, or if a measurement should be entirely discarded (see Section 2.2.3 for details).

The final statistical analysis between measured fluxes from differing size of chambers at the same location only included locations where none of the fluxes had rejected due to their respective decision algorithms. Fluxes for each chamber size were tested for normality (Kolmogorov-Smirnov) and homogeneity of variance (Levene's) before an appropriate test on the effect of chamber size and *post hoc* analyses. Following a method used in other systems where the size of sampling unit had been experimentally manipulated (Culp *et al.* 1994), the relationship between CH_4 flux variance and sample area was examined using a linear regression model.

4.3 Results

4.3.1 Comparison of diurnal CH_4 fluxes using continuous measurement system

4.3.1.1 Effect of different diurnal periods and vegetation types on CH_4 fluxes

All acceptable CH_4 flux measurements made during both four day campaigns in May and August/September 2010 are shown in Fig. 4.3 and Fig. 4.4, respectively, and reveal high temporal variability during short periods. For example, the low CH_4 flux during daylight hours on 24th May contrasted with the higher flux observed during the 22nd May. Net flux values were comparable with those obtained with a non-automated chamber (coverbox) method from a similar time of year in 2009 (see Fig. 2.2) as no single flux from any vegetation was higher than 2.5 mg CH_4 m^{-2} h^{-1}.

No diurnal pattern of CH_4 fluxes over time was apparent for any vegetation type and the non-parametric test on the difference between the summed day and night fluxes during the first campaign showed no significant difference between the median values (Wilcoxon signed-rank using PROC UNIVARIATE on SAS®, $p = 0.850$). Mean (±SEM) summed CH_4 fluxes over the first campaign were 1.483 (±1.458) mg CH_4 m^{-2} during the day and 2.030 (±1.969) mg CH_4 m^{-2} during the night. As with the seasonal CH_4 flux measurements at Vyrnwy during 2009 (Fig. 2.4), the comparison between different vegetation types showed sedge to be a particularly strong source of CH_4 (see Fig. 4.5) and vegetation did have a significant effect on CH_4 fluxes (Kruskal Wallis using PROC NPAR1WAY on SAS®, $p = 0.041$). The mean (±SEM) emission of CH_4 from sedge during the first campaign (15.539 (±12.686) mg CH_4 m^{-2}) was higher than any other vegetation (see Fig. 4.5), however, *post hoc* tests between sedge and the other three vegetation types were not significant (Wilcoxon rank sum using PROC NPAR1WAY and EXACT WILCOXON option on SAS® with a Bonferroni-corrected alpha value of 0.0167). Results for individual comparisons were $p = 0.100$ for sedge and grass, $p = 0.200$ for sedge and heather, and $p = 0.100$ for sedge and Juncus.

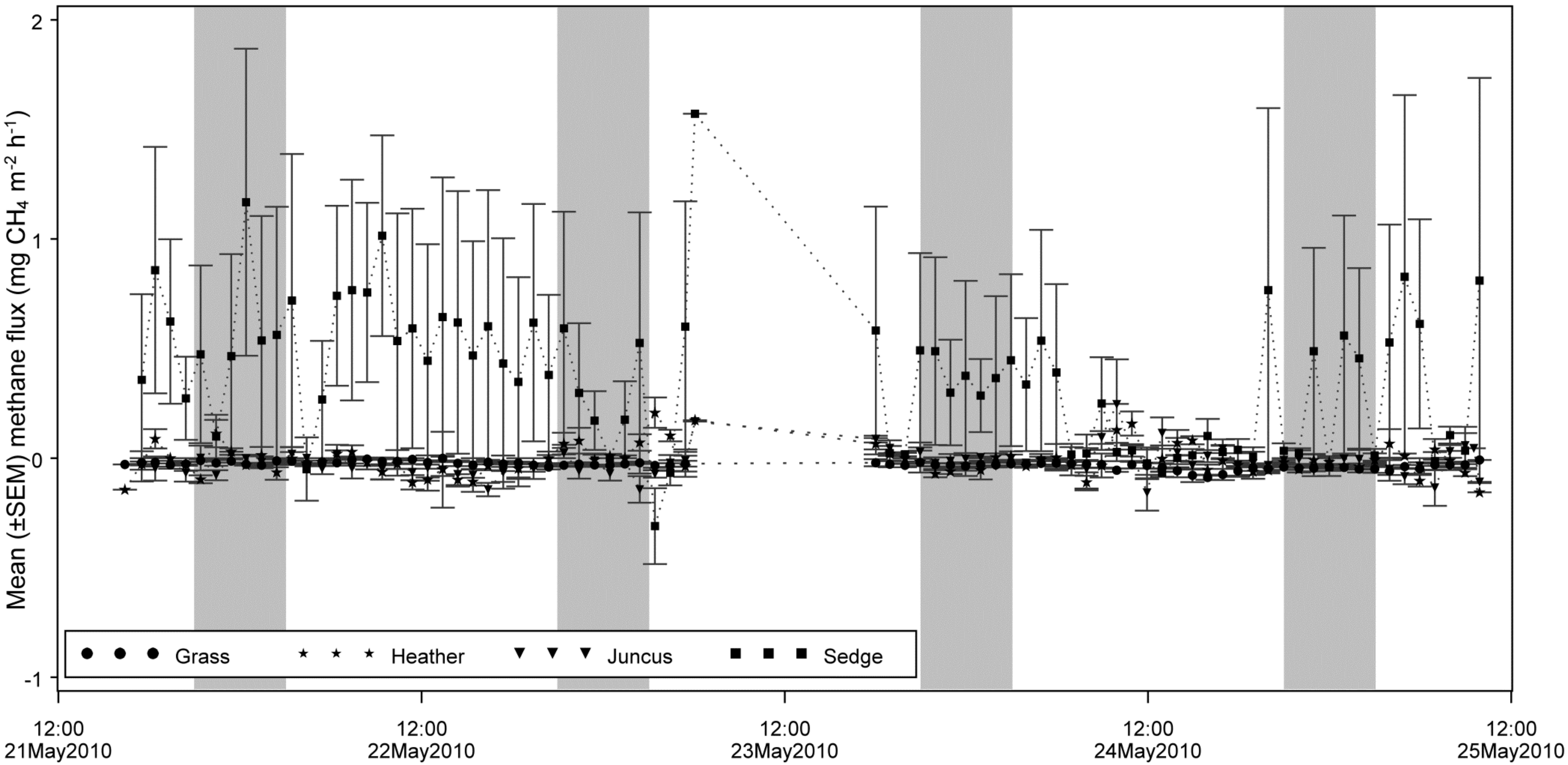

Fig. 4.3 Mean (±SEM) CH_4 flux (mg CH_4 m^{-2} h^{-1}) of each vegetation type for each hourly cycle of measurements during four days of near-continuous monitoring in May 2010. Where SEM is shown, n = 3. Dashed lines are for illustrative purposes only. Shaded areas indicated hours of darkness.

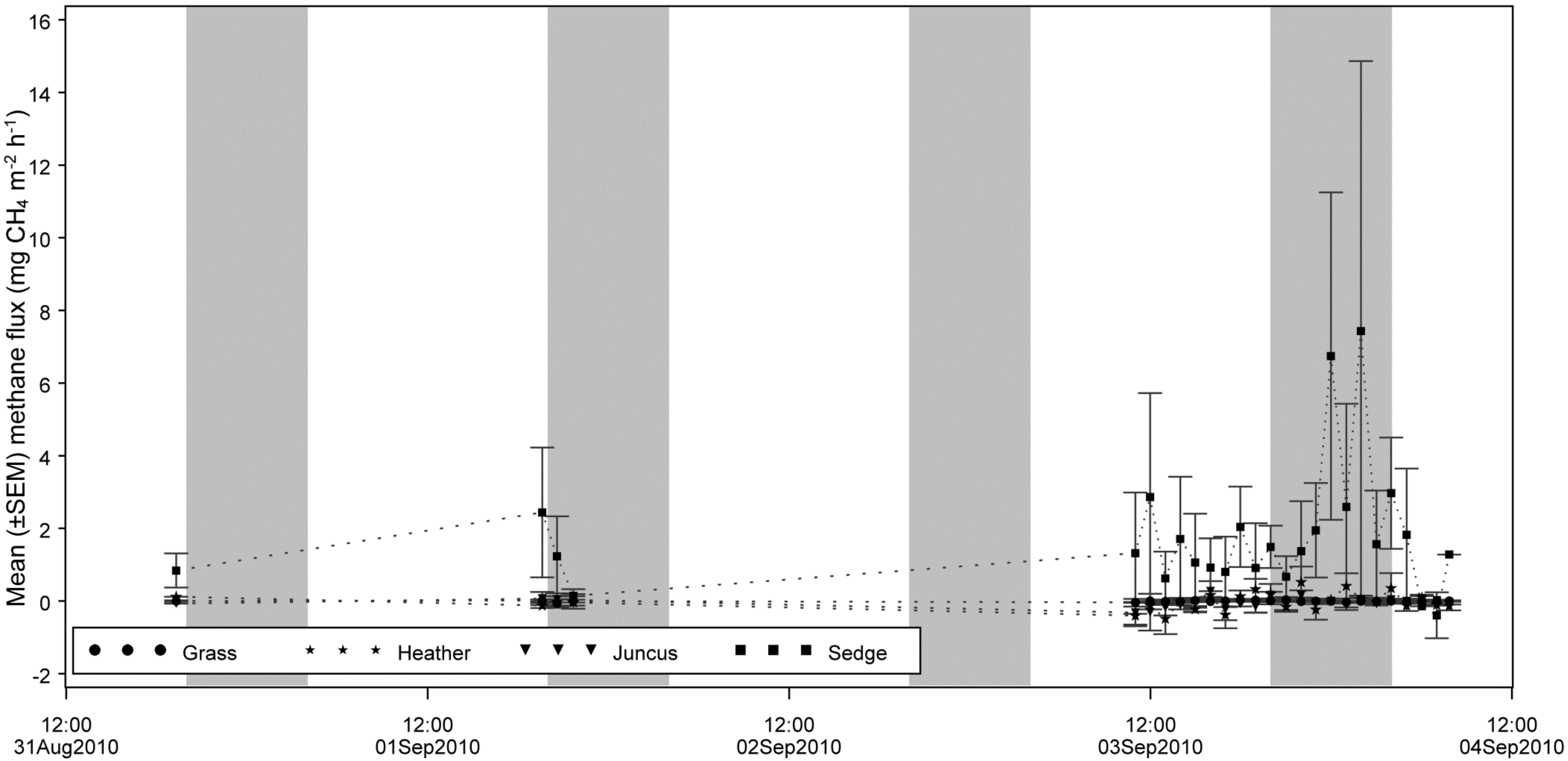

Fig. 4.4 Mean (± SEM) CH_4 flux (mg CH_4 m^{-2} h^{-1}) of each vegetation type for each hourly cycle of measurements during four days of near-continuous monitoring in August and September 2010 (see Fig. 4.3 for details). Shaded areas indicated hours of darkness.

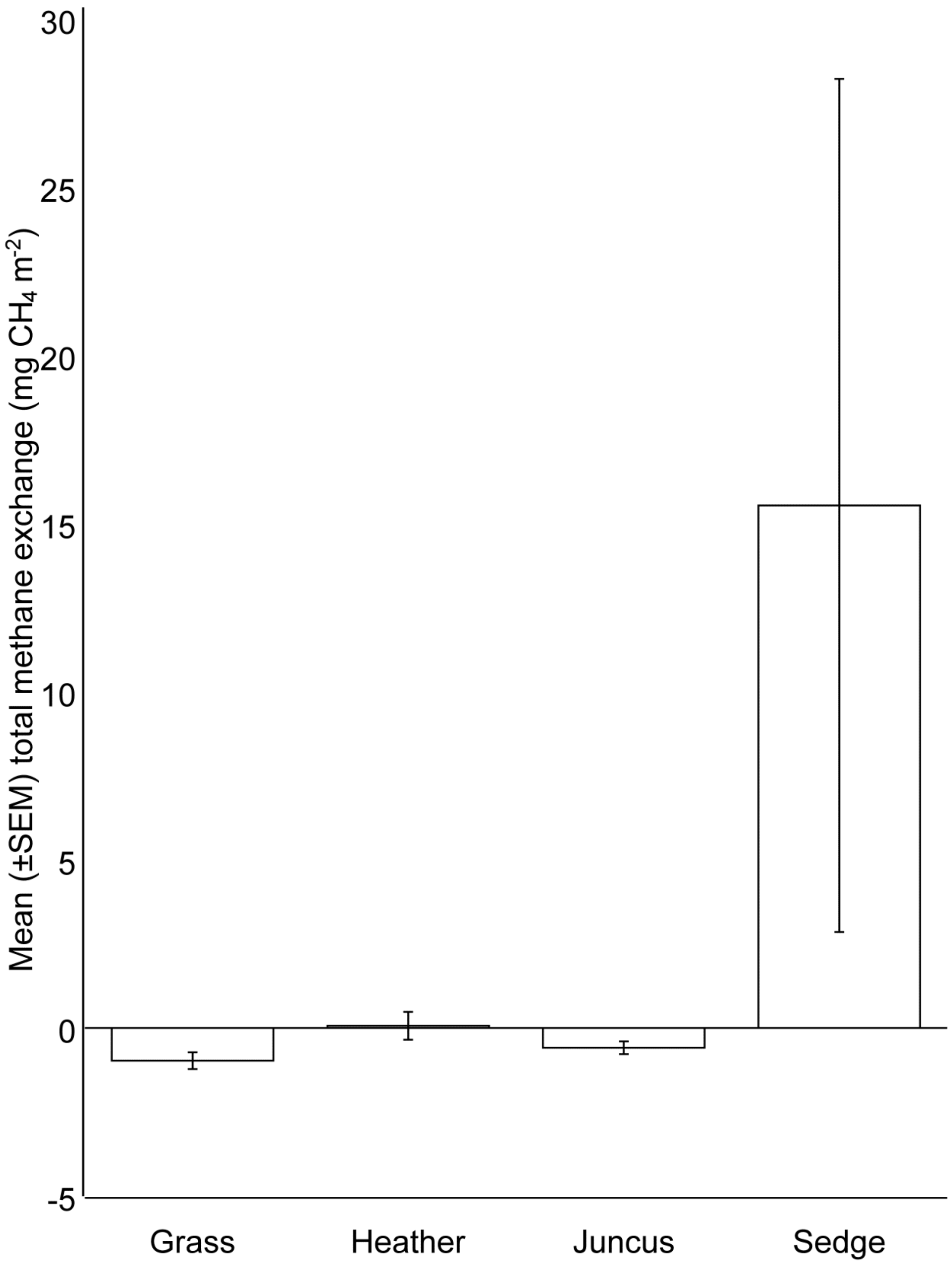

Fig. 4.5 Mean (± SEM) total CH_4 flux (mg CH_4 m^{-2}) for each vegetation type during four days of near-continuous monitoring in May 2010. There was a significant effect of vegetation on methane flux ($H(3) = 8.23$, $p = 0.041$) but *post hoc* pairwise comparisons (with Bonferroni corrections) between sedge and each other vegetation type were non-significant.

In comparison to 915 measurements made during the May 2010 campaign, only 284 CH_4 flux measurements were successfully made during the second campaign in August/September 2010, and only one 24-hour period was successfully monitored (see Fig. 4.4). However, fluxes from sedge sites were still notably larger than during May and were comparable with values obtained at a similar time of year during the seasonal study (see Fig. 2.2) with a maximum individual flux of 15.2 mg CH_4 m^{-2} h^{-1}. Mean (±SEM) summed daytime flux was 0.762 (±1.139) mg CH_4 m^{-2} h^{-1} and mean summed night-time flux was 4.673 (±3.478) mg CH_4 m^{-2} h^{-1}, but the difference between them was not significant (Wilcoxon signed-rank, $p = 0.052$). Vegetation did have a significant effect on CH_4 fluxes (Kruskal Wallis, $p = 0.038$) with sedge again producing the highest mean emission of CH_4 during the second campaign (see Fig. 4.6). However, as before, selective *post hoc* comparisons (Wilcoxon rank sum) between sedge and the other vegetation types were all non-significant (with grass, $p = 0.700$; with heather, $p = 0.100$; and with Juncus, $p = 0.100$).

4.3.1.2 Environmental data

Only plots of environmental variables during the first campaign are displayed, since the second campaign was limited to a single 24-hour period of flux measurements and considered too short a period to study temporal trends. The fine temporal resolution of measurements (Fig. 4.7) showed differing responses of soil temperature at sites dominated by different vegetation types, to diurnal variations in insolation and air temperature. For example, Juncus soil temperature showed very little diurnal response and, whilst the responses from grass, heather and sedge soil temperatures were all delayed, grass had a smaller amplitude and a more delayed response. No rainfall fell during the five days of flux measurement in May, 2010.

There was no obvious association between the high temporal variations seen in CH_4 fluxes (Fig. 4.3) and changes in environmental variables (Fig. 4.7) but the lower sedge fluxes that

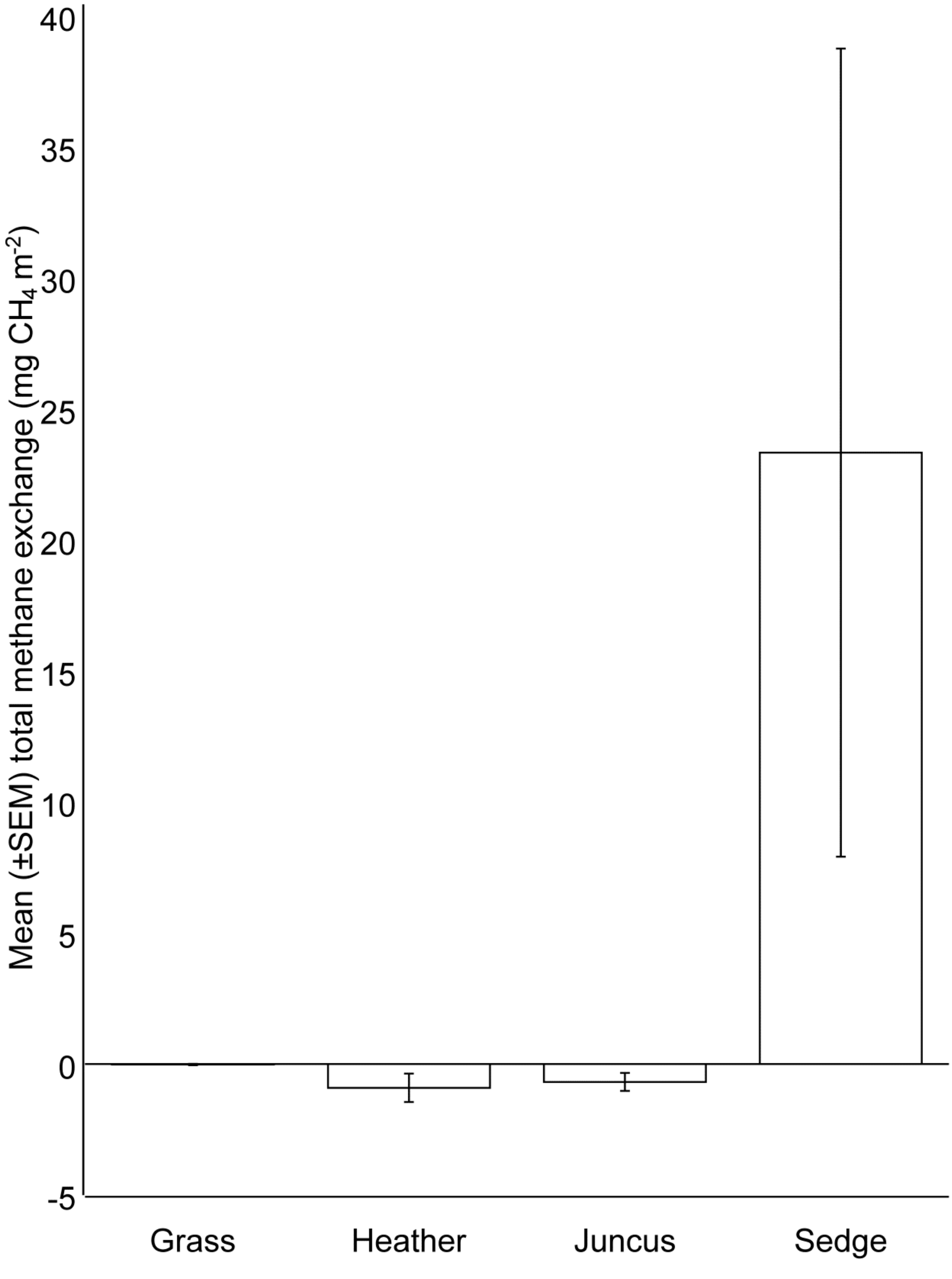

Fig. 4.6 Mean (± SEM) total CH_4 flux (mg CH_4 m^{-2}) for each vegetation type during four days of near-continuous monitoring in August and September 2010. There was a significant effect of vegetation on methane flux ($H(3) = 8.44$, $p = 0.038$) but *post hoc* pairwise comparisons between sedge and each other vegetation type were non-significant.

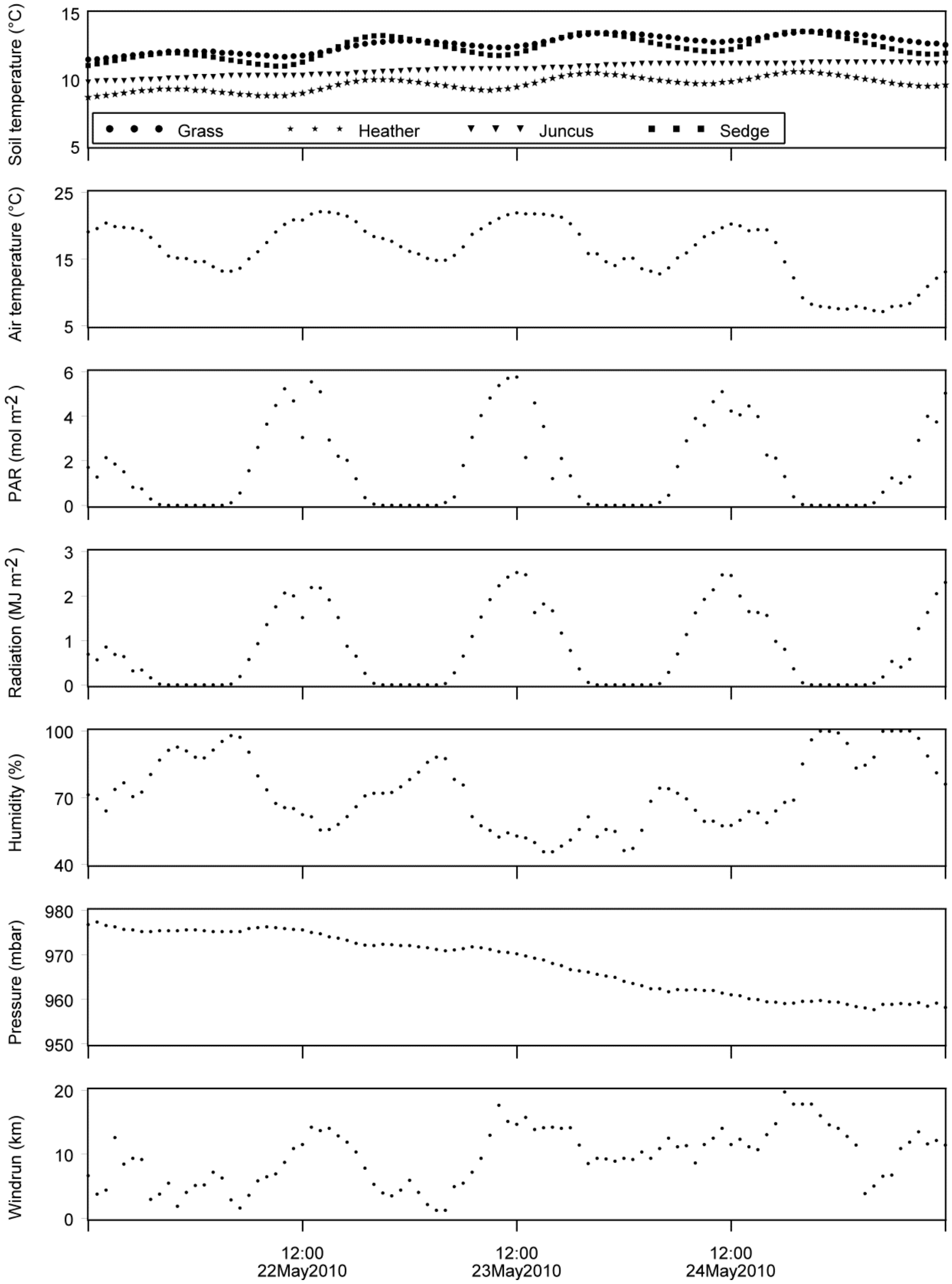

Fig. 4.7 Mean soil temperature (°C) measured at a 10 cm depth for four vegetation types, mean air temperature (°C), total PAR (mol m^{-2}), total solar radiation (MJ m^{-2}), mean humidity (%), mean air pressure (mbar), and wind run (km) measured hourly from 21st to 25th May 2010.

occurred during 24^{th} May coincided with falling atmospheric pressure and immediately prior to a decrease in air temperature and increase in humidity. The contrast between wind direction during two 24-hour periods of the 22^{nd} and 24^{th} May (Fig. 4.8) marked a change in dominant wind direction, from the SW during the 22^{nd} to the N and NW on the 24^{th}, and suggested a change in weather front and air mass over the site between these two days.

4.3.1.3 Regression between CH_4 flux and environmental variables

As in Section 3, in order to determine which environmental variables were controlling CH_4 fluxes, a series of regression models between fluxes and environmental variables were separately constructed for each vegetation type and for all data, regardless of vegetation. The initial approach used all environmental variables measured to the nearest quarter-hour to each flux measurement (referred to as concurrent measurements) as independent variables in multiple stepwise regression models. The results presented in Table 4.1 show air pressure was the only independent variable significantly related to CH_4 flux in the grass ($p<0.001$, $r^2 = 0.189$) and sedge models ($p=0.002$, $r^2 = 0.042$). Wind speed ($p<0.001$, $r^2 = 0.058$) was the first significant independent variable selected in the heather model, followed by soil temperature ($p=0.011$, $r^2 = 0.027$). Soil temperature was also the only significant independent variable selected by the Juncus model ($p=0.029$, $r^2 = 0.021$). When data from all vegetation types were combined in a single multiple regression model, soil temperature ($p<0.001$, $r^2 = 0.021$) was selected at the first step and air pressure ($p<0.001$, $r^2 = 0.018$) was selected at the second. Regardless of whether one or two significant independent variables were included, all models produced weak final r^2 values, the largest being 0.189 for grass.

The final series of regression models used the running average of environmental variables over varying periods prior to the point of flux measurement as independent variables.

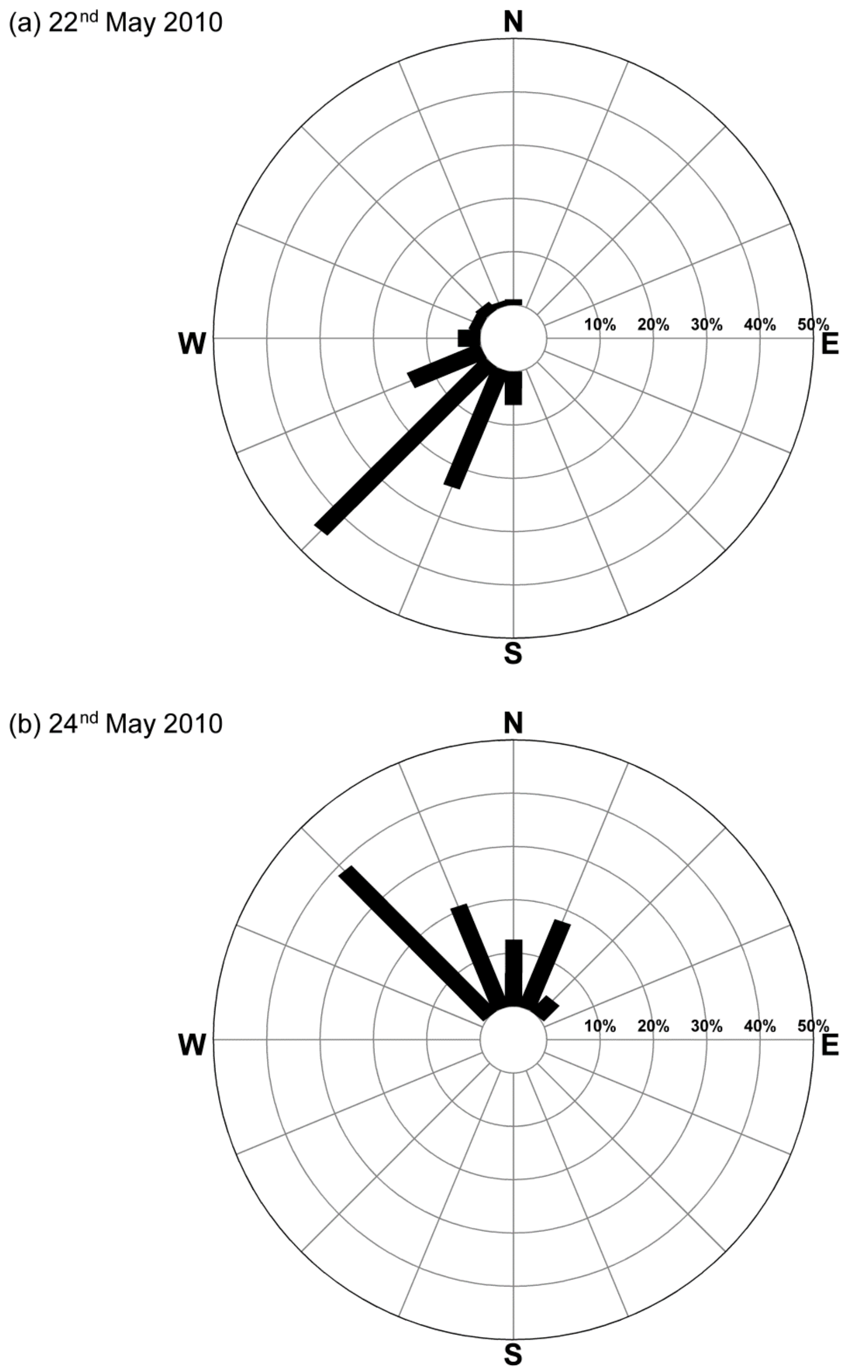

Fig. 4.8 Proportional wind direction (%), grouped by cardinal, primary intercardinal and secondary intercardinal directions, during two 24-hour periods (starting at 00:00) in May 2010.

Table 4.1 Results of multiple regressions between CH_4 flux and concurrent measurements of environmental variables for all data and for data subsetted by vegetation type (grass, heather, Juncus and sedge).

Step and parameters	CH_4 flux				
	Grass	**Heather**	**Juncus**	**Sedge**	**All**
First step					
Independent variable	Air pressure	Wind speed	Soil temp	Air pressure	Soil temp
β	0.002	-0.022	0.030	0.020	0.050
r^2	0.189	0.058	0.021	0.042	0.021
p	<0.001	<0.001	0.029	0.002	<0.001
Second step					
Independent variable		Soil temp			Air pressure
β		0.029			0.007
r^2		0.027			0.018
p		0.011			<0.001
Final model					
Intercept (β)	-1.543	-0.239	-0.342	-18.543	-7.716
r^2	0.189	0.084	0.021	0.042	0.039
p	<0.001	<0.001	0.029	0.002	<0.001

Running average values were used, from the nearest quarter-hour (0 hours) increasing in 15 minute intervals up to running averages from the preceeding 10 days (240 hours). As in Section 3.3.3 (Fig. 3.17 and Fig. 3.18), single regression models were constructed for each environmental variable for all running averages, and the r^2 values produced by each regression model (that used running averages from 0 to 240 hours) are shown in a single plot. Each plot shows all r^2 values for each combination of dependent (all data, or subsetted by vegetation type) and independent variables (soil temperature, air temperature, PAR, solar radiation, humidity, wind speed, rainfall and air pressure).

In contrast to the analysis with seasonal CH_4 fluxes (see Section 3.3.3), Fig. 4.9 and Fig. 4.10 show that, when compared to models using concurrent measurements, r^2 values were not greatly increased when running averages were used. Also, no progression in-to and out-of phase was observed for any environmental variable but plots were similar to the undefined patterns produced when random simulated data was used to test this form of analysis. The absence of a steadily moving pattern suggested that the subsequent approaches to multiple regression between CH_4 fluxes and running averages of environmental variables in Section 3.3.4 were not useful with this short-term, high temporal resolution data set.

4.3.2 Impact of chamber area on apparent flux

The proportion of measurements from the Perspex chambers which were rejected by the flux algorithm due to excessive leakage (38.9%) was higher than from the cloche (0%) and contributed to the result that, from 12 original locations, only two locations had successful measurements with all sizes of chamber. To ensure a suitable number of replicate measurements from all chamber sizes at the same locations were obtained, the original flux algorithm (described in Section 2.2.3) was altered to accept larger amounts of chamber leakage (down to 25% of the initial headspace concentration). Results from the adjusted

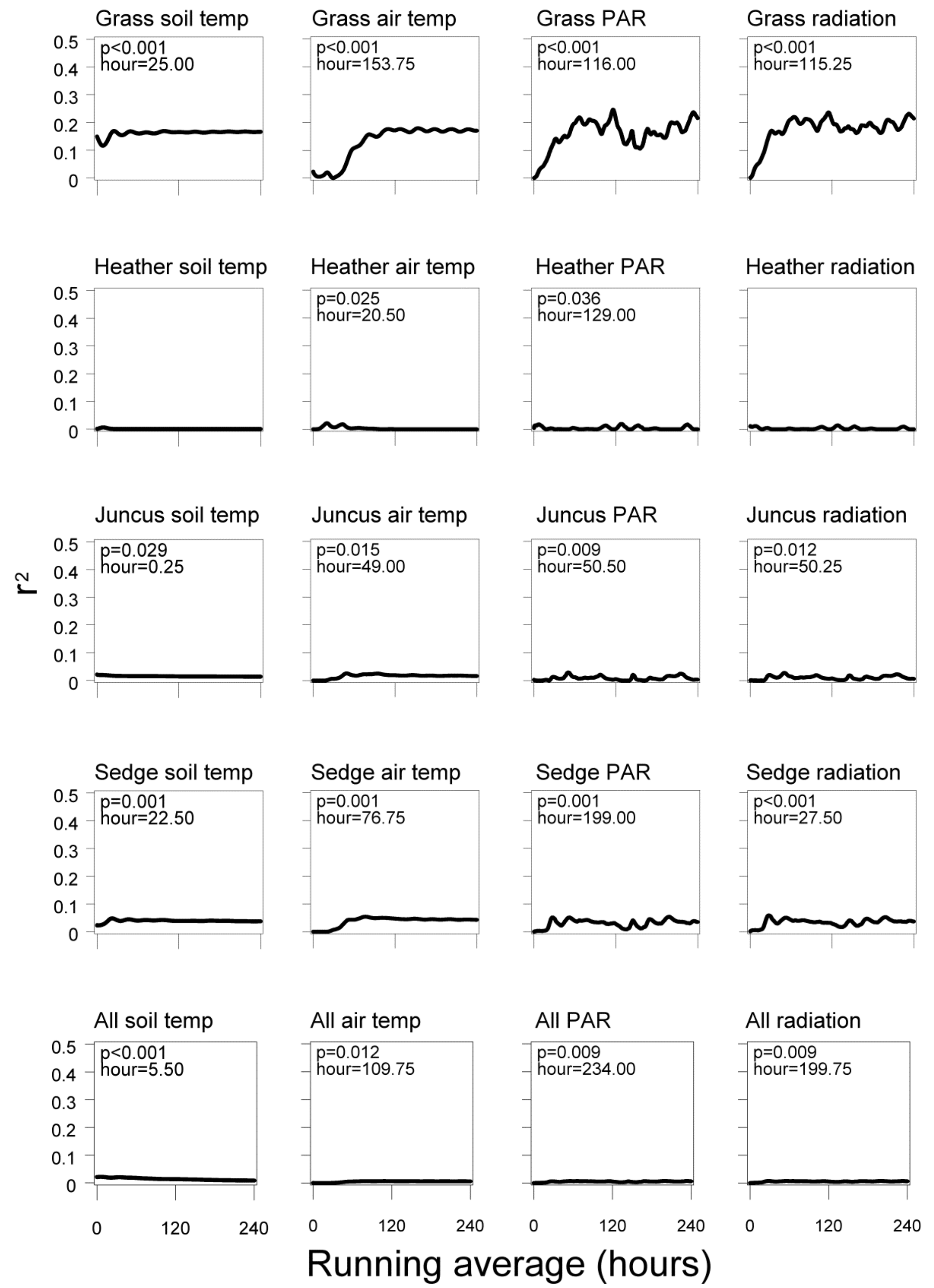

Fig. 4.9 Results (r^2 values) from a series of regression models between CH_4 fluxes of each vegetation type (dependent variable) and the running average of each environmental variable over 0 to 240 hours prior to flux measurement (independent variable: soil temperature, air temperature, PAR and solar radiation). If significant, the most significant p value, and period of running average (day), are annotated on the plot.

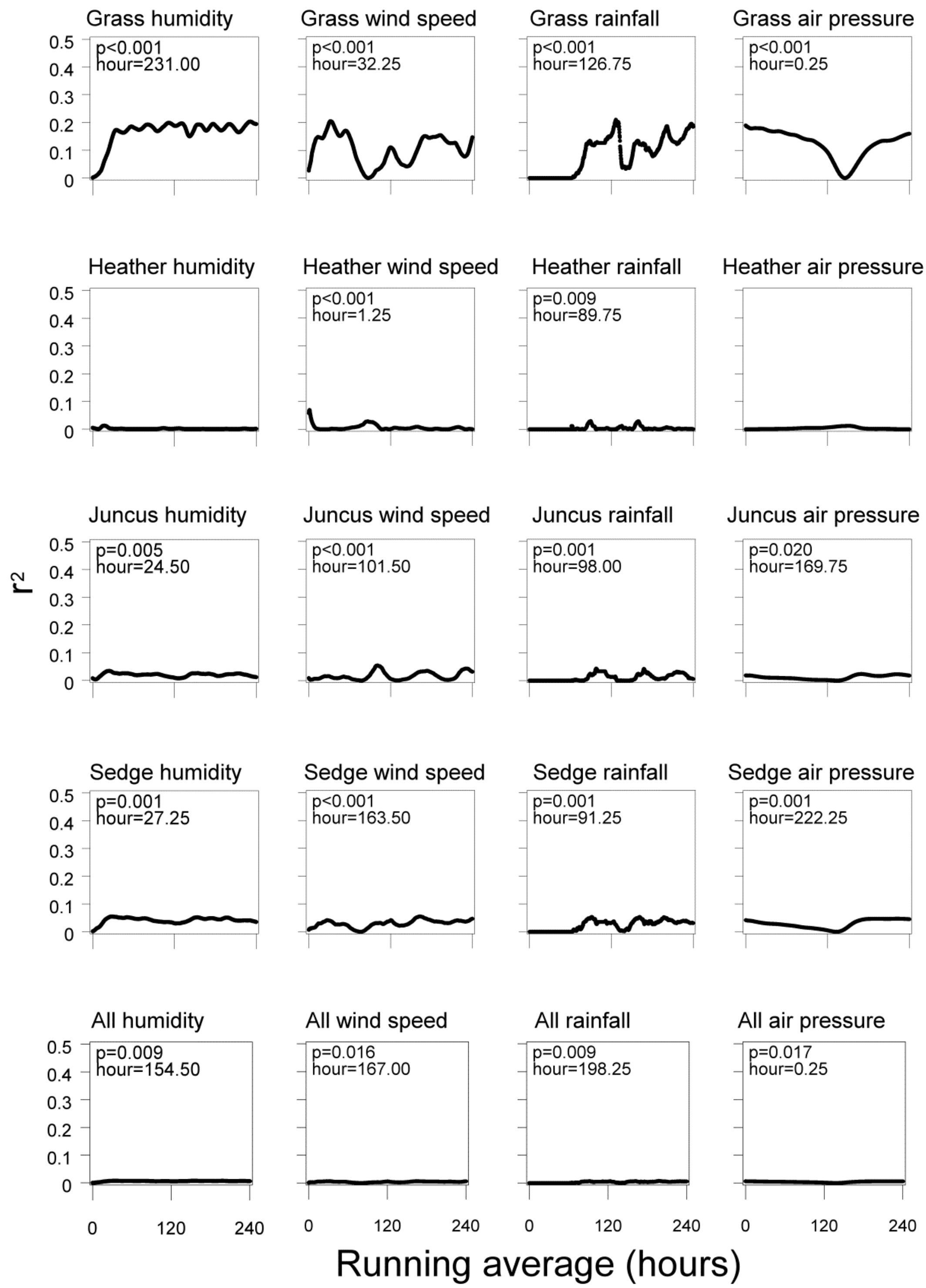

Fig. 4.10 Results (r^2 values) from a series of regression models between CH_4 fluxes of each vegetation type (dependent variable) and the running average of each environmental variable over 0 to 240 hours prior to flux measurement (independent variable: humidity, wind speed, rainfall and water table; see Fig. 4.9).

flux algorithm showed that CH_4 fluxes ranged from 0 to 8.491 mg CH_4 m^{-2} h^{-1} for 10 cm chambers, 0 to 5.140 mg CH_4 m^{-2} h^{-1} for 30 cm chambers, 0 to 3.981 mg CH_4 m^{-2} h^{-1} for 90 cm chambers, and 0.963 to 8.571 mg CH_4 m^{-2} h^{-1} for cloches.

The mean (±SEM) CH_4 flux from all locations and chamber sizes was 3.574 (±0.479) mg CH_4 m^{-2} h^{-1} compared to a mean flux of 3.529 (±1.673) mg CH_4 m^{-2} h^{-1} from all heather and sedge sites during the seasonal study in August 2009 (see Fig. 2.2).

When only CH_4 fluxes from locations measured with all chamber types were used, mean fluxes (±SEM) for each chamber size were: 3.215 (±1.871) mg CH_4 m^{-2} h^{-1} for 10 cm chambers, 2.226 (±1.152) mg CH_4 m^{-2} h^{-1} for 30 cm chambers, 2.650 (±0.9319) mg CH_4 m^{-2} h^{-1} for 90 cm chambers, and 4.710 (±0.402) mg CH_4 m^{-2} h^{-1} for cloches (see Fig. 4.11). Using location as a block effect, chamber size did not have a significant effect on CH_4 fluxes (Friedman's ANOVA using PROC FREQ CMH2 options on SAS®, $p = 0.209$), but a primary feature of the results was the marked reduction in SEM as larger chambers were used. Results from the linear regression model showed that the standard deviation of CH_4 fluxes was significantly correlated with the $\log_{10}$ of the area within each chamber ($p = 0.019$, see Fig. 4.12) with an r^2 value of 0.961.

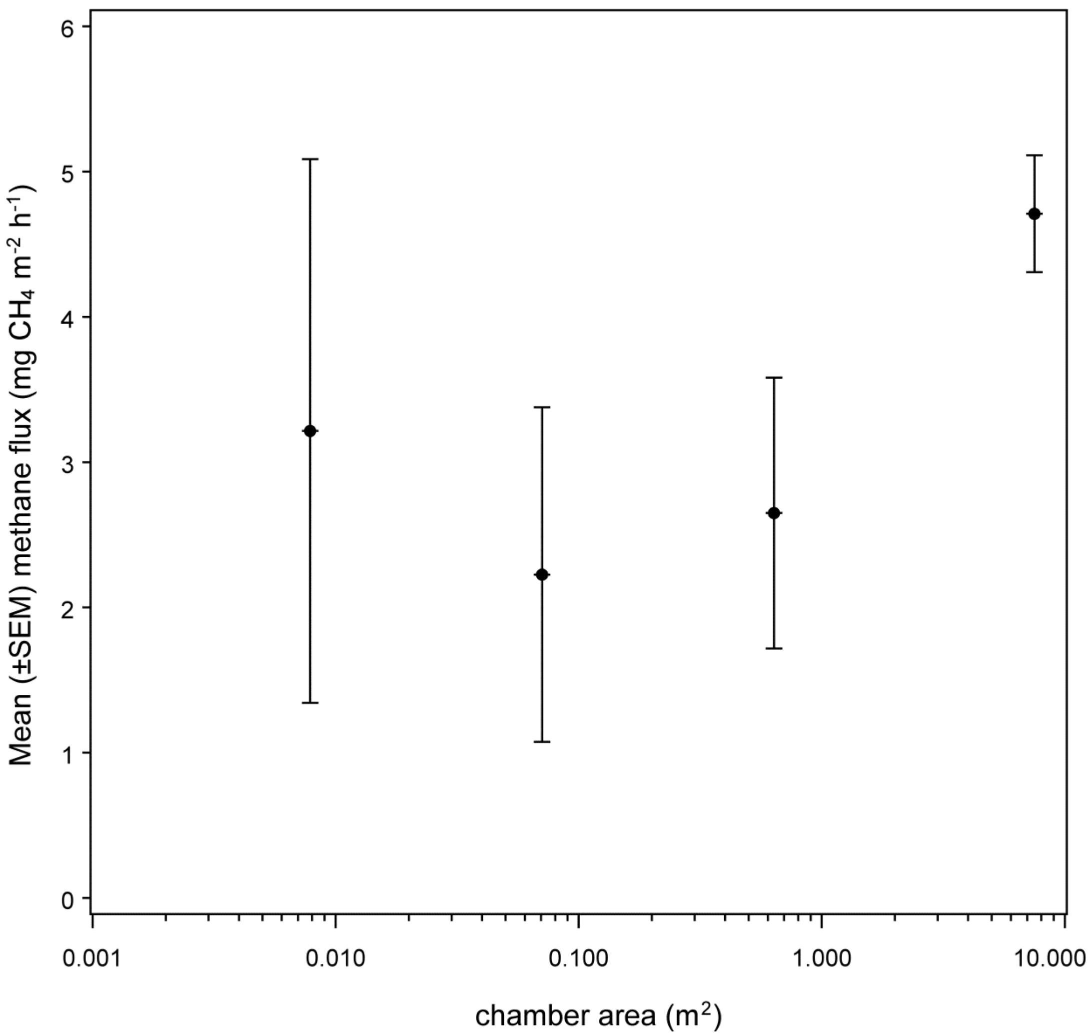

Fig. 4.11 Mean (± SEM) CH_4 flux measurement (mg CH_4 m^{-2} h^{-1}) of chambers with different sized areas (m^2). Flux measurements were made at the same locations and within one hour of each other. Note the log_{10} scale on the x-axis.

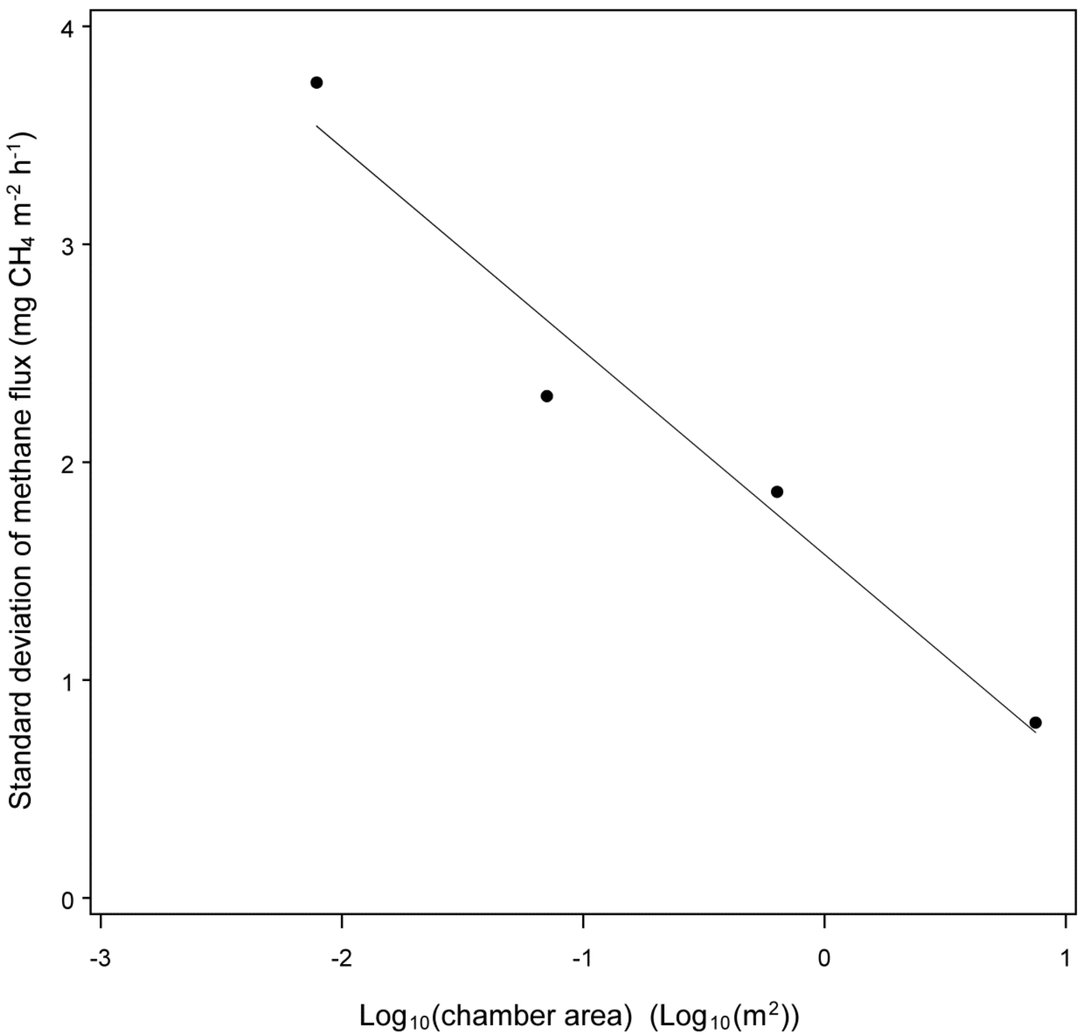

Fig. 4.12 Relationship between the standard deviation of mean CH_4 flux (mg CH_4 m^{-2} h^{-1}) and the $\log_{10}$ of the area within each chamber ($\log_{10}$ (m^2)). Results from a linear regression model were significant (p = 0.019) with an r^2 value of 0.961.

4.4 Discussion

4.4.1 Comparison of diurnal CH_4 fluxes

The development of a system to automatically measure multiple replicates of CH_4 fluxes from sites with taller vegetation (see Section 4.2.1.2) enabled near-continuous monitoring of CH_4 fluxes in a blanket bog. These measurements revealed no significant difference between fluxes measured during the day and night, a result that, combined with the absence of repeatable diurnal pattern, suggests that studies that are limited to measuring CH_4 flux in daylight hours (for example, see Section Chapter 2) are representative of other times of the day. Strong diurnal patterns have been observed at sites with vegetation that produce pressurized flow-through (Lambers *et al.* 1998) of gases in aerenchyma, since insolation can result in an internal pressure gradient within the aerenchyma and, consequently, higher CH_4 fluxes during the day (Chanton *et al.* 1993). In contrast, diurnal patterns are also evident at sites where diurnal changes in soil temperature produces stronger fluxes between 22:00 - 24:00 hours (Laine *et al.* 2007). Soil temperature was found to be a significant controller of CH_4 fluxes at heather and Juncus sites during the May campaign, but never explained more than 3% of the variation in CH_4 fluxes (Table 4.1). This suggests that, as observed at other ombrotrophic peatlands in the UK (Greenup *et al.* 2000), the absence of diurnal pattern is because neither pressurized flow-through or immediate response of methanogenic and methanotrophic populations to changing soil temperature occurred at these sites.

The variability of the sedge fluxes during May 2010 does suggest that infrequent measurements of CH_4 fluxes, such as weekly or monthly sampling typical of chamber-based measurements, may not be representative of CH_4 fluxes in the intervening periods. For example, estimates of CH_4 fluxes from sedge for the month of May based on simple multiplication, extrapolated from single CH_4 flux measurements, would be 330.5 mg CH_4 m^{-2}

month^{-1} if measurements were made 12:00 on the 22nd May, but -17.58 mg CH_4 m^{-2} month^{-1} had measurements been made 48 hours later. An alternative method of extrapolation uses regression models relating CH_4 fluxes to controlling environmental factors. Long-term, or large scale, records or predictions of controlling environmental factors can subsequently be used to extrapolate estimates of CH_4 fluxes over larger temporal or spatial scales (Becker *et al.* 2008; Koehler *et al.* 2011). However, this approach is only appropriate if CH_4 fluxes are found to be strongly associated with specific environmental variables. Unfortunately, the maximum amount of variation that could be explained by concurrent environmental variables in this study was 18.9%, being less than 5% for Juncus and sedge (Table 4.1). No hysteresis (*sensu* Section 3.4.3) in the response of CH_4 fluxes to environmental conditions was observed for any combination of vegetation and environmental variable so conditions immediately prior to the time of flux measurement did not appear to control CH_4 fluxes. The low r^2 values produced from this study (Fig. 4.9, Fig. 4.10 and Table 2.1) may be a result of the limited variation of values used in models during such a short time period: had sampling incorporated greater seasonal variation in CH_4 fluxes and environmental conditions (temperature, radiation etc.), relationships may have been more significant (Dinsmore *et al.* 2009a). However, results from this study suggest that if simple linear methods of extrapolation are to be used to estimate CH_4 fluxes over a longer time period, sampling needs to be more frequent than monthly or weekly to better represent the natural temporal heterogeneity of CH_4 fluxes from the blanket bog at Lake Vyrnwy.

In addition to examining fine scale temporal trends of CH_4 flux, results from this study also showed significant differences in CH_4 fluxes between vegetation types at this site. The higher mean emission of CH_4 from sedge during both measurement campaigns confirms the effect of aerenchymous plants observed elsewhere (Greenup *et al.* 2000), although the CH_4 fluxes from Juncus were no different from sites dominated by non-aerenchymous vegetation (Fig. 4.5 and Fig. 4.6). The IKONOS classification of the site at Lake Vyrnwy

(Fig. 2.7) and the map of the site (Fig. 2.1) show that Juncus dominates at lower elevations close to streams. In contrast, the Juncus measured during this study was growing on a ridge and was relatively dry. Mean (±SEM) water table depth measured manually at frequent occasions from 15/05/2010 and 26/05/2010 at each collar was -41.9 (±0.3) cm from the surface, in contrast to a mean of -7.12 (±0.17) cm observed by Wilson *et al.* (Wilson *et al.* 2011b) at sites close to streams and drains. As all the sampling in the current study was spatially limited to a single site, there is no expectation that Juncus will produce similar fluxes at other locations at Lake Vyrnwy, or at other blanket bog sites.

4.4.2 Impact of chamber area on apparent flux

Comparisons between different scales of CH_4 measurement are typically made using varied measurement techniques, such as micrometeorological approaches, including Eddy Covariance (EC), and chambers (Riutta *et al.* 2007; Forbrich *et al.* 2011). Comparisons using this approach either show CH_4 flux measurements to be comparable (Schrier-Uijl *et al.* 2010) or considerably different (Sachs *et al.* 2010): such conflicting results may be a result of differences in scale of variation within a landscape, method of measurement, or method of extrapolation. Homogeneous landscapes, where the proportions of landforms enclosed within a measurement area reflect the proportions of the wider landscape (such as in Forbrich *et al.* 2011), tend to be more comparable. In contrast, heterogeneous landscapes. which include more variable quantities and strengths of CH_4 sources in each measurement footprint (such as those in Teh *et al.* 2011; Baldocchi *et al.* 2012), tend to have larger differences in apparent flux when using different scales of measurement.

Standard statistical comparisons between direct measurements are normally not possible, as micrometeorological methods are not usually replicated in the same independent manner as for chambers, comparisons often resulting between the mean and variance of a number of chambers and a single integrated value from EC method (for example, see Fig. 5

in Clement *et al.* 1995; or Fig. 2 in Schrier-Uijl *et al.* 2010). In contrast, the results of the current study, with balanced comparisons of the effect of chamber area on CH_4 fluxes, showed no significant difference in apparent CH_4 flux at Lake Vyrnwy despite the sample area within each chamber type varying by over three orders of magnitude (Fig. 4.11). As any differences in methods of measurement or extrapolation were minimised or, in the case of the three sizes of Perspex chambers, entirely removed, this showed that any effects of scale did not significantly alter CH_4 flux estimates. This suggests there was no discernable bias associated with the chamber edge, such as the impact of root cutting during collar insertion on CO_2 fluxes (Heinemeyer *et al.* 2011) or lateral diffusion and leakage into and out of the chamber headspace (Hutchinson and Livingston, 2001), which would have increased as the ratio chamber edge to sampling area in the smaller diameter chambers increased. The care taken over shallow insertion of collars, and use of SF_6 and N_2O to correct for leakage, may have reduced any such bias in this study.

In addition to testing the effect of sample area on apparent CH_4 flux, the current study also revealed a strong negative relationship between sampling area size and standard error of the mean for estimates of CH_4 flux (Fig. 4.12). This has two implications with regard to the spatial distribution of CH_4 fluxes at the study site: (i) As demonstrated with other ecological phenomena (Bellehumeur *et al.* 1997), the reduced variation from larger chambers clearly demonstrated that CH_4 fluxes occurred at spatially heterogeneous rates. Specifically, as CH_4 flux (mg CH_4 m^{-2} h^{-1}) was an average measure of CH_4 exchange from each chamber, any extreme 'hotspots' (Becker *et al.* 2008) of CH_4 production or oxidation included within larger chambers will be "diluted" within the average flux. In contrast, the inclusion or exclusion of hotspots with smaller chambers results in more variable flux measurements. This result contrasts with predictions that the mean and variability will remain constant as sampling size increases in a spatially homogeneous landscape (Bellehumeur *et al.* 1997). (ii) Standard error still increased as chamber area decreased below 0.07 m^2 which also suggested the scale (Dungan *et al.* 2002) of spatial heterogeneity of CH_4 fluxes was smaller than 0.07 m^2, i.e. the size of the hotspot of CH_4 activity was smaller than 0.07 m^2.

The cause of the hotspots in CH_4 activity was not identified during the current study but there are several possible reasons for this observed heterogeneous distribution. Whilst all vegetation can function as a provider of substrate for CH_4 emission (Whiting and Chanton, 1993), one specific functional group of plant species, including sedges and rushes, can provide aerenchymous structures that function as a conduit of CH_4 from the sub-soil to the atmosphere (Clymo and Pearce, 1995). The relative abundance of members of this functional group may contribute to the strength of CH_4 emission. The site used for the current study initially appeared to be a homogeneous mix of heather and sedge vegetation, with a ubiquitous covering of *Sphagnum* spp., yet quantitative estimates of the proportional coverage of heather for each measurement location showed marked differences. It was also observed that sites with a higher coverage of (non-aerenchymous) heather had a lower coverage of (aerenchymous) sedge, and *vice-versa*. Regression models showed there was no significant relationship between CH_4 flux and heather coverage for any of the different sized chambers (0.008 m^2, $p = 0.919$; 0.07 m^2, $p = 0.789$; 0.6 m^2, $p = 0.204$; 7.5 m^2, $p = 0.666$). The lack of significant relationship with heather coverage, particularly for the smallest chambers that had displayed the highest variation in estimates of the mean CH_4 flux (Fig. 4.12), suggests that small scale variation in aerenchymous plant structures was not the factor driving hotspots of CH_4 activity. Other putative candidates, which were not examined during the current study, are small-scale spatial variations in abiotic factors, including soil hydrology (Becker *et al.* 2008), or biotic factors such as soil invertebrates and their associated gut-fauna which includes methanogens (Konig, 2006). Craneflies are a dominant soil invertebrate species in blanket bogs in the UK (Carroll *et al.* 2011) and whilst studies of their gut-flora are limited, Rogers and Doran-Peterson (2010) have shown cranefly species are capable of digesting lignocellulose as a result of the diverse microbial communities present in the fermentation chamber of their gut. The identification of the underlying reasons for hotspot of CH_4 activity could enable appropriate stratification of the blanket bog and, consequently, a more representative estimate of landscape flux.

A common feature of all current studies presented here was the large standard error (SEM) of the mean CH_4 fluxes (Section 4.3.1.1, Fig. 4.11, Fig. 3.25 and Fig. 3.26). As well as highlighting the heterogeneous nature of CH_4 fluxes at Lake Vyrnwy, such large variability of estimates increased the difficulty in distinguishing between different treatments, whether relating to the time of day that measurements were made, size of chamber used, or the large-scale blocking of drains. Whilst statistical comparisons were possible, the lack of significance in each of these studies does not provide convincing answers to the questions about temporal and spatial variation.

4.4.3 Summary

Hourly measurements of CH_4 flux showed high variability but no significant difference between measurements during day and night. Flux estimates were made using chambers with footprints that varied by three orders of magnitude and there was no significant effect on mean CH_4 fluxes. However, the variance of CH_4 flux estimates strongly correlated with sample area with markedly smaller variance as chamber size increased. This result revealed features of the spatial variation of CH_4 fluxes, but also suggests that, when large numbers of replicates are not available, the use of larger chambers in future studies could considerably reduce variability in flux estimates and help identify any subtle differences in treatments.

Chapter 5 General Discussion

5.1 Peatlands as a source of CH_4

Despite the expectation that northern peatlands function as net emitters of CH_4 (Worrall *et al.* 2007b), observations of CH_4 oxidation at blanket bogs are not uncommon (Clymo and Pearce, 1995; Fowler *et al.* 1995b). The drainage of the blanket bog at Lake Vyrnwy over the last 40 years (Wilson *et al.* 2010), and the high variability of CH_4 fluxes in other peatland sites (McNamara *et al.* 2008) lead to uncertainty in any assumptions about the net direction of CH_4 flux at the blanket bog used in the current study. The observation that the blanket bog around Lake Vyrnwy is a net source of CH_4 is therefore important (Table 2.1) and matches reported estimates from similar sites in the UK (Fowler *et al.* 1995b; McNamara *et al.* 2008). Whilst sampling in the current study was deliberately stratified to measure CH_4 fluxes from a range of vegetation types, a constraint on the estimate of landscape flux was the spatial limitation of observations. Specifically, all measurements were made at the tops of ridges and none were taken in water courses or pools. Only a small proportion of the total area at the Lake Vyrnwy site is covered by water courses or pools yet they may provide 'hotspots' of CH_4 emission (*sensu* Becker *et al.* 2008) due to the domination of anoxic conditions and increased ebullition of CH_4 from the soil to the atmosphere (Kellner *et al.* 2006). Without measurements at these microsites, their relative contribution to the landscape CH_4 flux is unknown, but as permanently (or generally) flooded sites, it can be assumed they increase, rather than decrease, any annual estimate of CH_4 flux to the atmosphere.

Scaling up the best annual estimate (±SEM) of CH_4 flux from the current study at the Lake Vyrnwy site during 2009 of 9.8 (±3.8) g CH_4 m^{-2} $year^{-1}$ would produce an annual estimate for upland peatlands in the UK of 0.2 (±0.08) Tg CH_4 $year^{-1}$ assuming that the 20530 km^2 of similar peatland estimated by Cannell *et al.* (1999) produced the same CH_4 flux. This estimate of peatland CH_4 flux represents the major natural terrestrial emissions from the UK, as emissions from wild ruminants and termites can be considered negligible (Verkerk and Bravery, 2001; Wuebbles and Hayhoe, 2002); this figure is equal to 10% of the estimated 1.9 Tg CH_4 $year^{-1}$ for all anthropogenic CH_4 emissions in the UK during 2003 (Baggott *et al.* 2005). Additional uncertainty in any UK estimate of peatland CH_4 flux is derived from uncertainties in the area of the UK covered by peatlands with estimates ranging from 14790 to 29209 km^2 (Worrall *et al.* 2007b). Extrapolating from the current study, these large differences would change the relative CH_4 emission of peatlands to between 7.6% and 15.1% of anthropogenic CH_4 emissions. Parties to the United Nations Framework Convention on Climate Change (UNFCCC) have not been required to include 'natural' carbon emissions (such as those from peatlands) in National Inventory Reports (Cannell *et al.* 1999) but CH_4 emissions from upland peatlands are large, despite only covering between 6.6% and 13% of the terrestrial area in the UK (Milne and Brown, 1997; Worrall *et al.* 2007b).

5.2 Hysteresis

In addition to estimates of overall landscape CH_4 fluxes, the examination of spatial and temporal patterns of CH_4 flux in the current study emphasised several important factors. One interesting temporal feature was the repeated evidence of hysteresis in the response of CH_4 fluxes to changing environmental conditions. The existence of an autumnal 'shoulder of activity' in observed seasonal patterns of fluxes (Fig. 2.2), a feature which has been found in other published studies, but frequently not discussed (Ward *et al.* 2007), gave an initial indication that CH_4 fluxes do not simply respond to concurrent seasonal conditions. This lack of immediate response was emphasised by the low proportions of the variation in seasonal CH_4 fluxes that were explained by concurrent environmental variables (Table 3.1), and even lower proportions when trying to explain hourly measurements (Table 4.1). The positive relationship between depth to water table and CH_4 flux (Table 3.1; with CH_4

emission increasing as depth to water table increased) was an observation which conflicted with the expected response of CH_4 flux to water table (Le Mer and Roger, 2001) but could also be explained by the existence of hysteresis (Fig. 3.27). This unexpected response can also be seen from the work of others but has been left undiscussed (Bellisario *et al.* 1999; McNamara *et al.* 2008; Dinsmore *et al.* 2009a), and explained using alternative hypotheses. One hypothesis was the function of water table above the surface as a barrier to substrate provision for methanogenesis (Strack *et al.* 2004) or as a barrier to the transport of CH_4 through aerenchymatic structures of vascular plants (Sachs *et al.* 2010) but this was not supported by the current study as water table rarely moved above the soil surface long enough to inhibit plant productivity (Fig. 3.3 to Fig. 3.6) and the positive relationship was only observed at sub-sites dominated by non-aerenchymous heather vegetation (Table 3.1). The hypothesis that a deepening depth to water table may cause a release of CH_4 previously stored at lower depths of soil (Nykanen *et al.* 1998; Treat *et al.* 2007) was also not supported by the current study as monthly manual measurements of water table were never less than 15 cm from the surface, and relatively shallow when compared to measurements from other vegetation types. The absence of automated measurements and subsequent lack of fine-scale temporal changes in water table prohibited the detailed examination of the effect of water table movement on CH_4 fluxes and, consequently, satisfactory assessment of this alternative hypothesis in the current study.

An additional result from the current study which supported the hysteretic response of CH_4 flux to environmental conditions came from the detailed examination of this relationship between CH_4 fluxes and the running averages of environmental conditions prior to the point of measurement (Fig. 3.17 to Fig. 3.24). The progression 'in to' and 'out of' phase of results from numerous regression models (see Section 3.4.3 for details) demonstrated that temperature and radiation prior to the day of flux measurement exerted more control over

CH_4 fluxes than the same measurements made at the same time as the flux measurements. This approach was not always successful in identifying controls as this influence could not be found when examining the relationship between hourly CH_4 fluxes and environmental conditions (Fig. 4.9 to Fig. 4.10). This may have been a result of the limited seasonal range in CH_4 fluxes and environmental conditions that was observed, and/or the limited period that environmental conditions were measured prior to the point of CH_4 flux measurement: 10 days for the hourly study, compared to 180 days for the seasonal study. Whilst requiring a site with potentially extensive pre-existing records of environmental variables, the use of environmental variables prior to the point of CH_4 flux measurement may help to increase the predictive power of CH_4 flux models.

5.3 Multiple controls

A number of apparently significant environmental controls on CH_4 flux were identified in the current study, varying according to vegetation type, the frequency and length of the study of CH_4 fluxes, and whether relationships were calculated with concurrent or running averages of preceding environmental variables. For example, during the 14 month seasonal study (see Chapter 3) there was a significant relationship between CH_4 fluxes from sedge sites and concurrent measurements of soil temperature and humidity ($p < 0.001$, $r^2 = 0.415$, Table 3.1), but also between the running averages of soil temperature, solar radiation and water table prior to the day of flux measurement (with a maximum r^2 of 0.493, $p<0.001$, Table 3.2). In addition, there was a significant relationship between CH_4 fluxes and concurrent measurements of air pressure ($p = 0.002$, $r^2 = 0.042$, Table 4.1) when hourly measurements were made over a four day period (see Section 4.3.1). These apparently conflicting results may be a result of different measurements being used as independent variables in the different regression models for each study; in the seasonal study soil temperature, air temperature, PAR, solar radiation, humidity, wind speed, rainfall and manual water table measurements were used in the concurrent regression models, whereas soil temperature, solar radiation and modelled water table were the only measurements used in the final combination of regression models using running averages (Section 3.2.3). The four day hourly study used the same measurements as the seasonal study with the exception of water table measurements and the inclusion of atmospheric pressure (Section 4.2.1.4). A mixture of results may also have been generated as a result of autocorrelation between independent variables used in the multiple regression models (Field and Miles, 2010) although subtle differences do exist between the diurnal patterns of similar measurements of temperature and radiation (Fig. 4.7). Alternatively, CH_4 fluxes may be controlled by a variety of processes as suggested by results from repeated studies carried out at the same locations (e.g. compare Saarnio *et al.* 1997; and Becker *et al.* 2008). As suggested by Levy *et al.* (2012), these conflicting results, and relatively low proportion of variability in CH_4 fluxes explained by environmental variables (Table 3.1 and Table 4.1), may also be the result of a general low association between the measured variables and actual variables which directly influence the production, oxidation and transport of CH_4.

The use of running averages of environmental variables in single regression models showed a unimodal period of maximum control prior to the day of flux measurement, the specific period depending on the combination of vegetation type and environmental variable (Fig. 3.17 and Fig. 3.18). The use of more than one running average of environmental variables in multiple regression models showed two periods of control such as the preceding 60 days (where soil temperature controls a large amount of variation in CH_4 flux) and the preceding 150 days (where solar radiation is important, see Fig. 3.19). The asymmetrical shape of seasonal CH_4 fluxes (Fig. 2.2) also supports the existence of two such periods of control since fluxes did not correspond with seasonal patterns of any single environmental variable (Fig. 3.3 to Fig. 3.15). Whilst this study suggested the existence of two periods of control, the specific method of control could either be different periods of hysteresis in response to two changing environmental variables as suggested by Updegraff *et al.* (2001), or the differing hysteretic responses of methanogens and methanotrophs to changes in the same environmental variable, as suggested by Macdonald *et al.* (1998). The use of pulse-labelled $^{13}CH_4$ to measure rates of CH_4 oxidation, in contrast to net CH_4 flux, has been undertaken at the same Lake Vyrnwy site. Results are not yet available (Subke, personal communication) but the study will produce seasonal measurements of relative rates of CH_4 oxidation and production, hopefully unravelling how differing responses by methanogens and methanotrophs to changing environmental conditions may contribute to the distinctive patterns of net seasonal CH_4 flux.

5.4 High variability of CH_4 flux measurements

Several problems were highlighted during the current studies of CH_4 fluxes made at Lake Vyrnwy. The most consistent feature of results was the large error associated with virtually all estimates of mean CH_4 flux. Of all the estimates of CH_4 flux in Chapter 2, Chapter 3 and Chapter 4, the coefficient of variation (CV) was only reduced below 40% (Fig. 2.4, Table 2.1, Fig. 3.25, Fig. 3.26, Fig. 4.5 and Fig. 4.6,) when large chambers covering 7.5 m^2 of soil surface were used as part of the study of chamber area on apparent flux (CV of 17.1%; Fig. 4.11). These errors incorporate the inherent variation of observed CH_4 fluxes, which was emphasised by the low number of replicates, and any measurement errors. The temporal variability in the current study was high, whether measured at a seasonal (Fig. 2.2) or hourly frequency (Fig. 4.3, Fig. 4.4) and spatial variability was also very large, even after stratifying for vegetation, elevation or treatment of drains (Fig. 2.4, Fig. 3.25, Fig. 3.26 and Fig. 4.5). The use of environmental conditions to explain the variability observed in CH_4 fluxes showed that most unexplained variation was due to temporal, rather than spatial, variation (see Section 3.4.4), yet spatial variation was still high when compared to errors of vegetation classification (see Section 2.3.2).

The high variability in fluxes observed in this study confounds the sensitivity of experiments (*sensu* Hurlbert, 1984) designed to compare inherent differences in CH_4 flux due to vegetation types or management practices. This was evident in Chapter 2 where there was no apparent significant effects of vegetation type on fluxes (Fig. 2.4) despite an expected effect of the presence of aerenchymous vegetation (Greenup *et al.* 2000) and despite the similar comparison in Section 4.3.1 which showed a significant vegetation effect (Fig. 4.5). In addition, the apparent lack of effect on CH_4 fluxes from blocking of ditches (Section 4.3.2) may have been a consequence of the high variability in fluxes (Fig. 3.25) as drained sites were expected to have lower CH_4 emissions. There were no strong *a priori* expectations of diurnal cycles in CH_4 flux, with results from previous studies at other sites being contradictory (e.g. Fowler *et al.* 1995b; Greenup *et al.* 2000; Laine *et al.* 2007) but high variability may again have contributed to the lack of apparent difference between estimates of day and night CH_4 fluxes (Section 4.3.1.1).

An obvious solution to making measurements in highly variable systems is to increase the number of replicates to an appropriate level (Denmead, 2008), the over-arching constraints on increasing replicates are the resources required. This is particularly pertinent for *in situ* studies, such as all those in the current study, with inherent variation considered to be greater in such 'natural' field conditions when compared to more controlled *ex situ* laboratory studies. General restrictions in the current study included the resources required for CH_4 flux measurements in a relatively remote location, with more specific restrictions existing for each separate study. For example, co-located environmental variables were required for each CH_4 flux measurement due to the natural variation in environmental conditions across the site and necessitated the establishment of dedicated meteorological stations which subsequently restricted the numbers of replicates, and spatial coverage of sampling (Chapter 2 and 3). The establishment of a short-term continuous measurement system (Section 4.2.1) meant temporal variation in CH_4 flux was observable at an hourly scale, but also meant that replicates were limited by the number of independent chambers in the multiplexed system. The one study which, regardless of limitations of time and equipment, was still restricted by the ownership and management of the site itself was the *in situ* study of drain blocking (Section 4.2.2). Even when greater resources are available and studies of CH_4 flux conducted with larger numbers of replicates, variability of estimates can still be high. For example, the measurement of CH_4 fluxes at 21 sites, 10 of which were organic soils, by Levy *et al.* (2012) resulted in a mean CH_4 flux (± standard error of the mean, SEM) from all organic soil sites of 6.0 (±1.4) g CH_4 m^{-2} $year^{-1}$ with a high coefficient of variation (CV) of 75.9%.

One alternative to making *in situ* comparisons of CH_4 fluxes is the extraction and manipulation of samples in analogous laboratory-based studies with larger numbers of replicates and controlled uniform environmental conditions (Dinsmore *et al.* 2009b). However, the extraction and movement of samples may result in CH_4 fluxes being unrepresentative of typical field fluxes (Blodau and Moore, 2003a). Consequently, the explanatory or predictive power of such experimental results may not be directly applicable to the field system. An alternative solution is to design experiments without replication such as the "optimal impact study design" by Green (1979) which was a precursor to Before-After-Control-Impact approaches (BACI; Pitcher *et al.* 2009, *inter alia*) which are considered suitable for large scale manipulations requiring a single control and single treatment site. One early, successful example of this approach is the ecosystem scale manipulations at the Hubbard Brook Experimental Forest site which resulted in dramatic changes in dependent variables such as the concentration of NO_3^- (see Fig. 7 of Likens *et al.* 1970). However, without further replication, BACI approaches have been criticised for not being able to identify any inherent differences between control and treatment sites (Hurlbert, 1984), nor identify that sites may "drift apart" regardless of the imposed manipulation (Underwood, 1992). A final approach, which avoids the large scale replicated manipulations used in Section 4.2.2, is the *in situ* manipulation of conditions at a smaller scale. This may include small scale manipulation of conditions, such as the heating of 0.5 m^2 of soil with cables by Ineson *et al.* (1998) or 20 m^2 plots treated with passive warming systems (Beier *et al.* 2004). Limitations of smaller scale manipulations include unintended disturbances to conditions, which may increase as plot size decreases and edge effects increase (Beier *et al.* 2004), but in the context of the study at Lake Vyrnwy, also influence the acceptance of the results by stakeholders. Specifically, a consultation with stakeholders including farmers and land managers in the uplands around Lake Vyrnwy revealed that, regardless of how statistically rigorous the results may be, they would not be convinced by the results of a small scale experimental manipulation, preferring a landscape scale demonstration of the effect of any change in management (Ineson, personal communication).

An alternative approach, which reduced the variability of *in situ* CH_4 flux measurements and would increase the sensitivity of landscape scale manipulations, was the measurement of large areas or "footprints" of soil surface within a single chamber (Fig. 4.11). A single large footprint may enclose the same area as a larger number of small footprints but the reason for the low variability of estimates is subtly different. If a large number of randomly selected replicates are measured this will increase the likelihood of measurements being closer to the average flux, but it will also increase the denominator used to calculate the standard deviation of the estimate (Fowler *et al.* 1998). The use of fewer numbers of larger chambers results in a lower denominator (or fewer degrees of freedom) when calculating error terms, but variation (specifically, the sum of the squares of the deviations) is still reduced as a heterogeneous range of fluxes are averaged into a single flux. It may be expected that this effect is greater when making measurements in heterogeneous landscapes yet, despite clear recognition that CH_4 fluxes are spatially heterogeneous (Davidson *et al.* 2002), this has not been demonstrated previously for CH_4 fluxes. Despite emphasising the benefits of using chambers with large footprints, results from this study also demonstrate that, if used carefully, chambers with smaller footprints still produced an estimate of CH_4 flux which was not significantly different to those found using larger chambers (Fig. 4.11). Consequently, smaller chambers may still be preferable in some situations as they require fewer resources yet still produce reasonable estimates of mean CH_4 flux.

An implication from the study of different sized chambers (Section 4.3.2) is that the most sensitive way of measuring landscape scale manipulations is with the measurement of the largest possible footprint. In the case of direct measurement of surface CH_4 flux, the largest footprints are achieved using micrometeorological approaches, including eddy covariance (EC). EC measurements produce a single spatially integrated measurement from a footprint which is typically over "a few km^2" (Moncrieff *et al.* 1997) but are fixed to a single location, with any spatial comparisons being dependent on natural variations of wind direction and strength (Herbst *et al.* 2011) rather than through direct comparison. To satisfactorily compare several replicates of treatment and control sites with this technique several EC systems would be simultaneously required. Whilst data from increasing numbers of EC systems are collated into global observation networks (e.g. FLUXNET in Baldocchi *et al.* 2005), large numbers of EC systems are rarely used in single studies of landscape scale experiments. An alternative to several static measurement points is a highly mobile, airborne EC system, which can rapidly take measurements from large footprints in several landscape scale replicates, but is limited by topography and require plot sizes of multiple km^2 to calculate flux measurements (Hill *et al.* 2011).

5.5 Summary

In addition to emphasising the role of the UK uplands as an important source of CH_4, this discussion has highlighted several features which were repeatedly supported from the current studies. The first feature was hysteresis in the response of CH_4 fluxes to changing environmental conditions. This was something which could explain the 'inverse' relationship found between water table and CH_4 flux and which became evident when regressing running averages of environmental variables against measured CH_4 fluxes. Hysteresis was also one factor possibly contributing to the extended activity of CH_4 emission observed at the blanket bog around Lake Vyrnwy towards the end of 2009. The delayed response of CH_4 fluxes means that, rather than using concurrent environmental variables in regression studies which produce notoriously low proportions of variability of CH_4 fluxes, environmental variables temporally aggregated prior to the time of flux measurement can be used to improve the results of regression studies.

The second feature was the variety of environmental controls which were significantly related to CH_4 fluxes and the multiple periods of control by environmental conditions prior to the day of flux measurement. As a result of the production, oxidation and transport of CH_4 between the soil and atmosphere, it can be expected that a variety of environmental conditions contributed to the observed net CH_4 flux.

The final feature is the consistent high variability in virtually all estimates of CH_4 flux. Whilst this reflects the spatial heterogeneity of CH_4 fluxes, which in turn reflects small-scale variation in hydrological and thermal conditions, substrate provision, and availability of transport pathways, it also provides a constraint when attempting to compare different estimate of CH_4 flux. A novel approach for reducing variability of estimates was shown to be the use of chambers with very large footprints, although chambers with smaller footprints still provide useful data on the direction and magnitude of CH_4 fluxes.

Appendix A CH_4 headspace enhancement

There is an expectation that net CH_4 oxidation would not occur in an upland blanket bog due the dominance of anaerobic soils (Le Mer and Roger, 2001), with some models of CH_4 fluxes for UK uplands having no capacity for net CH_4 consumption to be incorporated under any circumstances (Worrall *et al.* 2007b). In direct contrast to this, observations from blanket bogs in the UK do actually report net oxidation to varying degrees (Fowler *et al.* 1995b; Macdonald *et al.* 1996; Macdonald *et al.* 1997). The protocol followed in the current study (Freitag *et al.* 2010) enabled the detection of net oxidation but has the potential to bias flux results by artificially enhancing oxidation in any anaerobic areas of soil, and by misinterpreting leakage of CH_4 from the headspace (specifically where the chamber meets the soil surface) as oxidation. Both these potential biases would result in increasingly negative flux measurements, lowering emissions or increasing oxidation. The development and availability of new technologies to measure CH_4 concentration (Fast Greenhouse Gas Analyzer (FGGA), Los Gatos Research, Mountain View, CA, USA) meant a comparison was possible between fluxes from enhanced and unenhanced headspaces using a cavity-enhanced absorption technique (Hendriks *et al.* 2008).

12 mesocosms, 25 cm diameter and 35 cm height, were extracted using a section of opaque PVC piping of the same dimensions from grass, heather and sedge vegetation types at Lake Vyrnwy (SH 93909 25871) for a retrospective study at the University of York. The mesocosms were extracted and returned to York on the 3rd March 2010 where they were stored externally for seven days with water tables maintained at the level observed in Lake Vyrnwy (16.3 cm, 9.7 cm and 5.3 cm below the surface for grass, heather and sedge, respectively), before fluxes were measured with and without headspace enhancement. All cores were measured using a non-steady state chamber, 25 cm diameter and 30 cm height, constructed in a similar way as described in Section 2.2.2, an important exception being the

addition of two ports: an inlet, positioned 2 cm above the base of the chamber, and an outlet, positioned 2 cm below the top of the chamber. Two 1 m sections of 3.2 mm internal diameter tubing (Bev-a-line IV, Thermoplastic Processes, Inc., Georgetown, DE, USA) were used to connect both ports to the FGGA so that once the chamber was sealed a closed loop between the FGGA and chamber was created. Rather than inserting a collar into the soil surface, the chamber was sealed to the exterior of the section of pipe used to extract the cores which had been left around each core. Using the internal pump of the FGGA at a rate of 55 ml s^{-1} and a sampling rate of 1 Hz, flux measurements were made for 15 minutes without CH_4 enhancement and, after a ten minute rest period with the chamber removed, another 15 minute measurement period with a headspace concentration of CH_4 enhanced to a mean (±SEM) of 29.6 (±1.1) ppm. Fluxes were calculated using the same decision algorithm as previously described and, as SF_6 had also been added to the headspace after closure and sampled from the chambers at 0, 5, 10 and 15 minutes, all fluxes were adjusted for leakage if necessary. Gas samples were extracted using a syringe, stored in 12 ml vials and analysed for SF_6 using a Perkin Elmer AutoSystem XL GC as described in Section 2.2.2.

Enhancing the ambient headspace concentration of CH_4, led to no significant difference in CH_4 fluxes for all mesocosms (Wilcoxon signed-rank, $p = 0.700$) nor was there an effect for each individual group of vegetation (grass, $p = 0.250$; heather, $p = 0.875$; and sedge, 0 = 0.250). There was a median reduction in CH_4 flux by 1.34 mg CH_4 m^{-2} h^{-1}, but the lack of difference in fluxes is seen as evidence that methane oxidation is not artificially enhanced by the levels of headspace enhancement used in the current study. The potential bias of misinterpreting loss of headspace concentration due to leakage being interpreted as net oxidation was avoided in the current study by the simultaneous addition of SF_6 and subsequent leakage adjustment by the flux algorithm. Overall, CH_4 flux measurements at Lake Vyrnwy do not appear to be more negative than other results when considering the range of measurements (mean fluxes -0.8 to 2.8 mg CH_4 m^{-2} h^{-1}) from other UK blanket bogs (Macdonald *et al.* 1998; Ward *et al.* 2007; McNamara *et al.* 2008; Hornibrook *et al.* 2009).

Appendix B Flux decision algorithm

CO_2 fluxes are not mentioned in the following section, but were calculated using an identical strategy as described for CH_4 fluxes. Fluxes were calculated using the slope of linear regression between CH_4 concentration and time for each individual coverbox and sampling. To remove the influence of erroneous data points (for example, as a result of faulty vial seal causing the leakage of a sample within a time series) and to provide a quality check for all 829 measurements, a decision algorithm was used to objectively and consistently determine how fluxes were calculated (see Fig. B.1 for CH_4 and Fig. B.2 for CO_2). The algorithm was designed to produce outcomes based on the following four sets of conditions:

(i) **Accept - no adjust.** Fluxes were calculated directly when a strong linear relationship (defined by $r^2 \geq 0.9$) between time and the headspace concentration of CH_4 was found. No adjustment for leakage was made if the SF_6 flux was either positive (Fig. B.1 and Fig. B.2; Outcomes 4, 7, 10, 14, 17 and 20), or because the apparent SF_6 change was 'effectively zero' (Outcomes 21, 24 and 26). 'Effectively zero' is defined as when the regression slope was not significantly different from zero (at the $p > 0.05$ level), the coefficient of variation was less than 30%, and the range of headspace concentrations was within a defined limit (0.01 ppm for SF_6). The flux (F, in mg CH_4 m^{-2} h^{-1}) was calculated as follows:

$$F = \left(\frac{\Delta \mathrm{C}}{\Delta \mathrm{t}} \cdot \frac{VT}{A}\right) \qquad (B.1)$$

where ΔC is the change of CH_4 concentration (ppmv) in respect to the change in time, Δt (hour) calculated with PROC REG and RSQUARE options in SAS® using the slope of the regression between concentration and time, V is an adjustment for headspace volume (dm^3), T is an adjustment for temperature (K), A is the surface area within the chamber (m^{-2}).

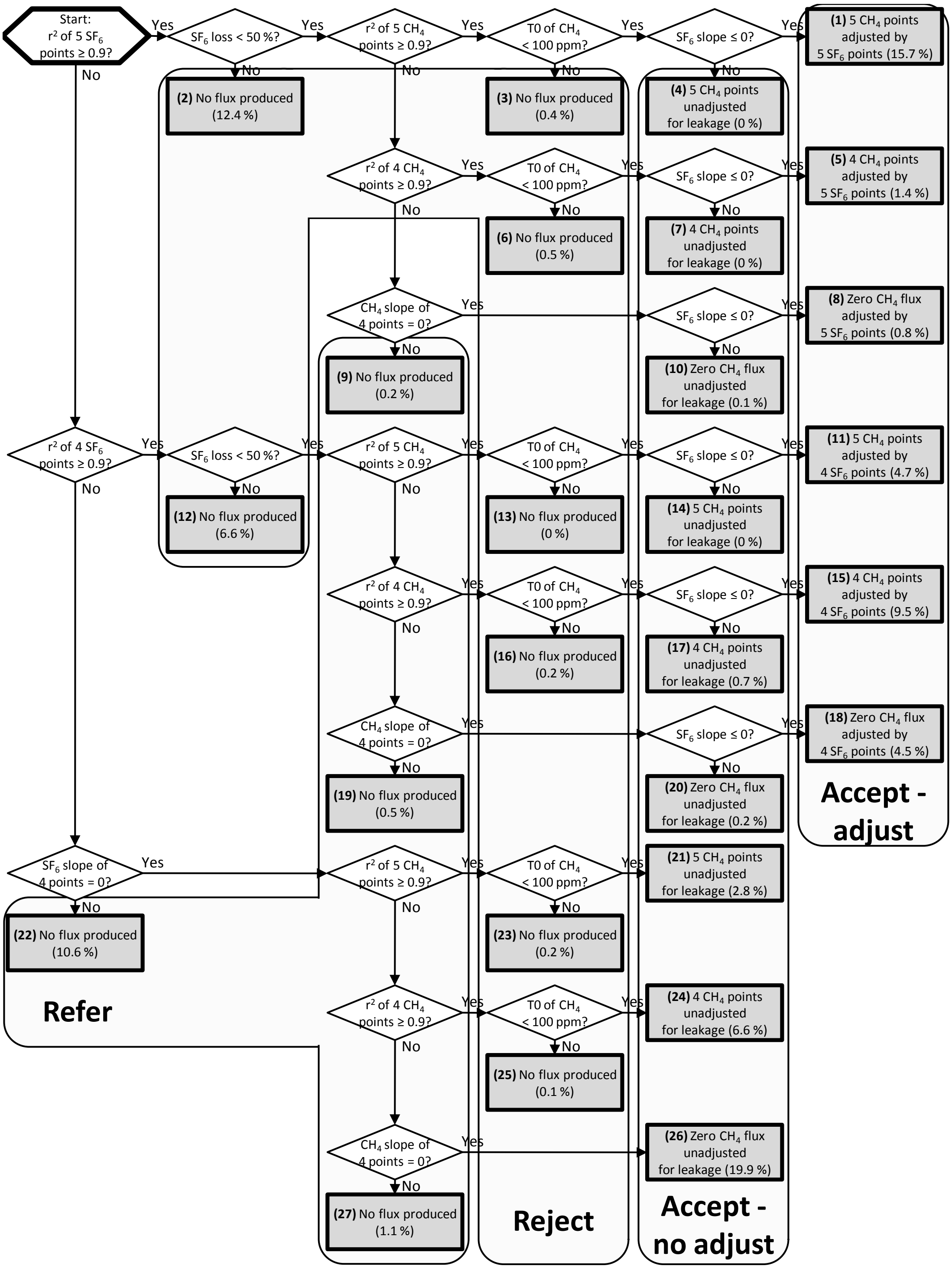

Fig. B.1 Schematic of the decision algorithm for CH_4 flux calculation. The 27 possible outcomes (numbered in bold), the proportion of decisions reached and four groups of required actions (refer, reject, accept and accept with leakage adjustment) are shown.

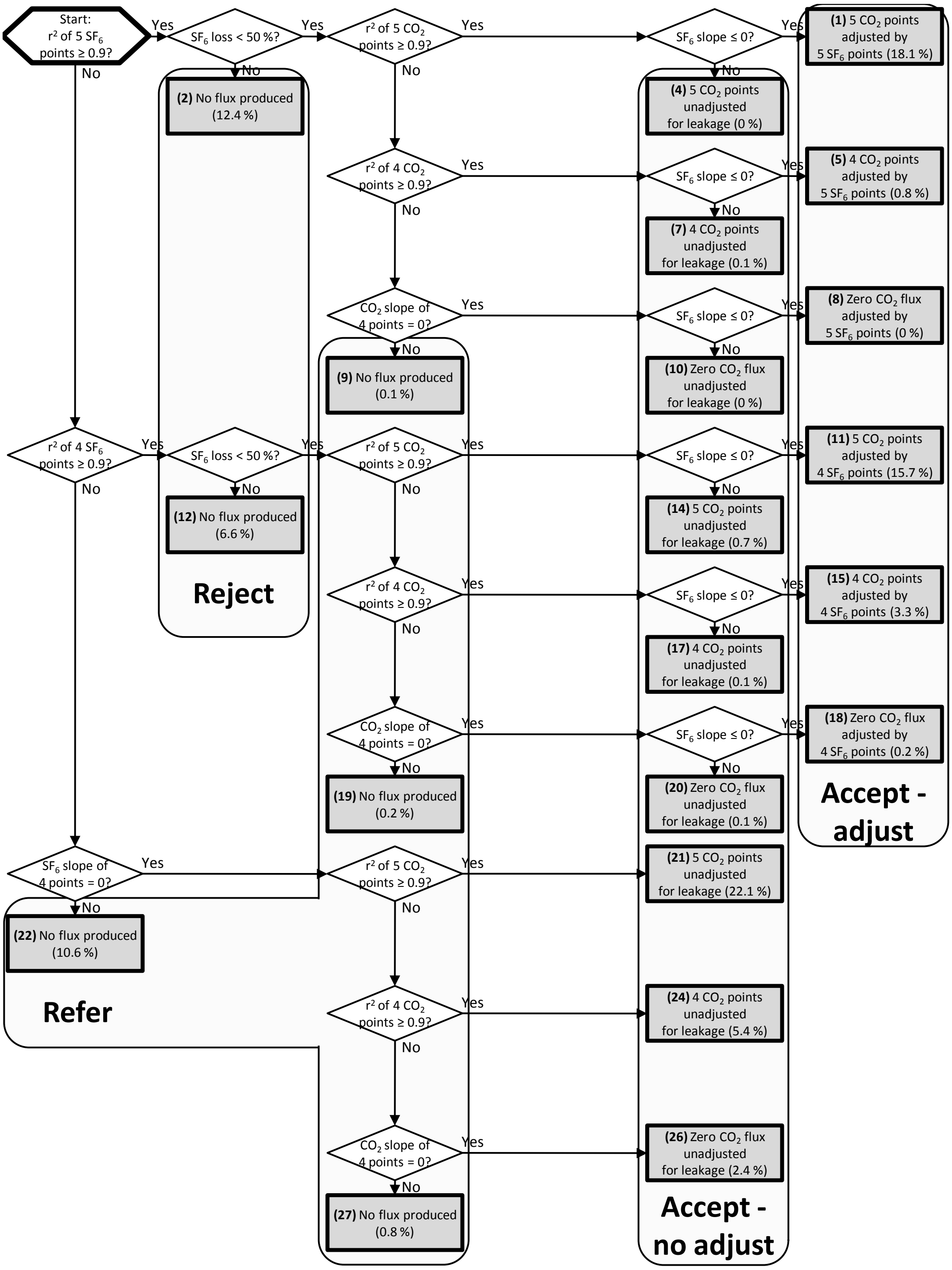

Fig. B.2 Schematic of the decision algorithm for CO_2 flux calculation. The 21 possible outcomes (numbred in bold), the proportion of decisions reached and four groups of required actions (refer, reject, accept and accept with leakage adjustment) are shown.

(ii) **Accept - adjust.** Fluxes were calculated as before but also adjusted for leakage when the headspace concentration of SF_6 declined in a strong linear manner (Outcomes 1, 5, 8, 11, 15 and 18). This combination of flux and leakage adjustment gave an emission rate of:

$$F = \left(\frac{\Delta C}{\Delta t} \cdot \frac{VT}{A}\right) + L \qquad (B.2)$$

where L is the following adjustment for leakage (mg m^{-2} h^{-1}):

$$L = \left(-\frac{\Delta S}{\Delta t} \cdot \frac{VT}{A} \times I\right) \qquad (B.3)$$

where ΔS is the change of SF_6 concentration (ppmv) in respect to Δt (hour), and I is the ratio of the CH_4 flux intercept to the SF_6 flux intercept (no units). In order to achieve an r^2 value above 0.9, occasionally one time point was removed from each series of five time points.

(iii) **Reject.** Measurements were rejected if an excessive leakage of headspace SF_6 (> 50% of the maximum concentration) occurred during the measurement period (Outcomes 2 and 12) or where the starting (T0) concentration of CH_4 was equal to or greater than 100 ppm (Outcomes 3, 6, 13, 16, 23 or 25).

(iv) **Refer.** The final component of the decision algorithm identified measurements with weaker linear relationships (where $r^2 < 0.9$) between time and the headspace concentration of CH_4 or SF_6, and where the apparent change in concentration was not effectively zero. These outcomes were signalled by the decision algorithm for further manually overseen examination (Outcomes 9, 19, 22 and 27). By altering the time point originally removed by the algorithm or, as was the case for 0.01% of calculations, the removal of two time points resulted in acceptance by the algorithm under the conditions of (i) or (ii).

The six examples of results shown in Fig. B.3 and Fig. B.4 represent six different outcomes from the decision algorithm produced in 71% and 69% of CH_4 and CO_2 flux calculations, respectively. Fluxes were produced from all the points in a time series and adjusted for chamber leakage for 16% of CH_4 and 18% of CO_2 flux measurements (for example see Fig. B.3 (a) where the CH_4 flux was 5.91 mg CH_4 m^{-2} h^{-1} and CO_2 flux was 818.3 mg CO_2 m^{-2} h^{-1}). The removal of one time point from a time series resulted in acceptable r^2 values for *ca.* 10% of CH_4 fluxes and 3% of CO_2 fluxes (for example see Fig. B.3 (b); rather than being rejected, a CH_4 flux of 0.07 mg CH_4 m^{-2} h^{-1} and CO_2 flux of 372.0 mg CO_2 m^{-2} h^{-1} were produced). Fluxes were produced from all points in a time series but not adjusted for chamber leakage in 3% of CH_4 fluxes and 22% of CO_2 fluxes (for example see Fig. B.3 (c); CH_4 flux of 3.59 mg CH_4 m^{-2} h^{-1}, CO_2 flux of 518.4 mg m^{-2} h^{-1}). Fluxes were discarded due to SF_6 leakage in 12% of all flux calculations (for example see Fig. B.4 (a)), or discarded due to low r^2 values in 11% fluxes (for example see Fig. B.4 (b)). The decision algorithm was directed to produce 'zero' fluxes in 20% of CH_4 fluxes and 2% of CO_2 fluxes (for example see Fig. B.4 (c), CH_4 flux of 0 mg CH_4 m^{-2} h^{-1}, CO_2 flux of 0 mg CO_2 m^{-2} h^{-1}).

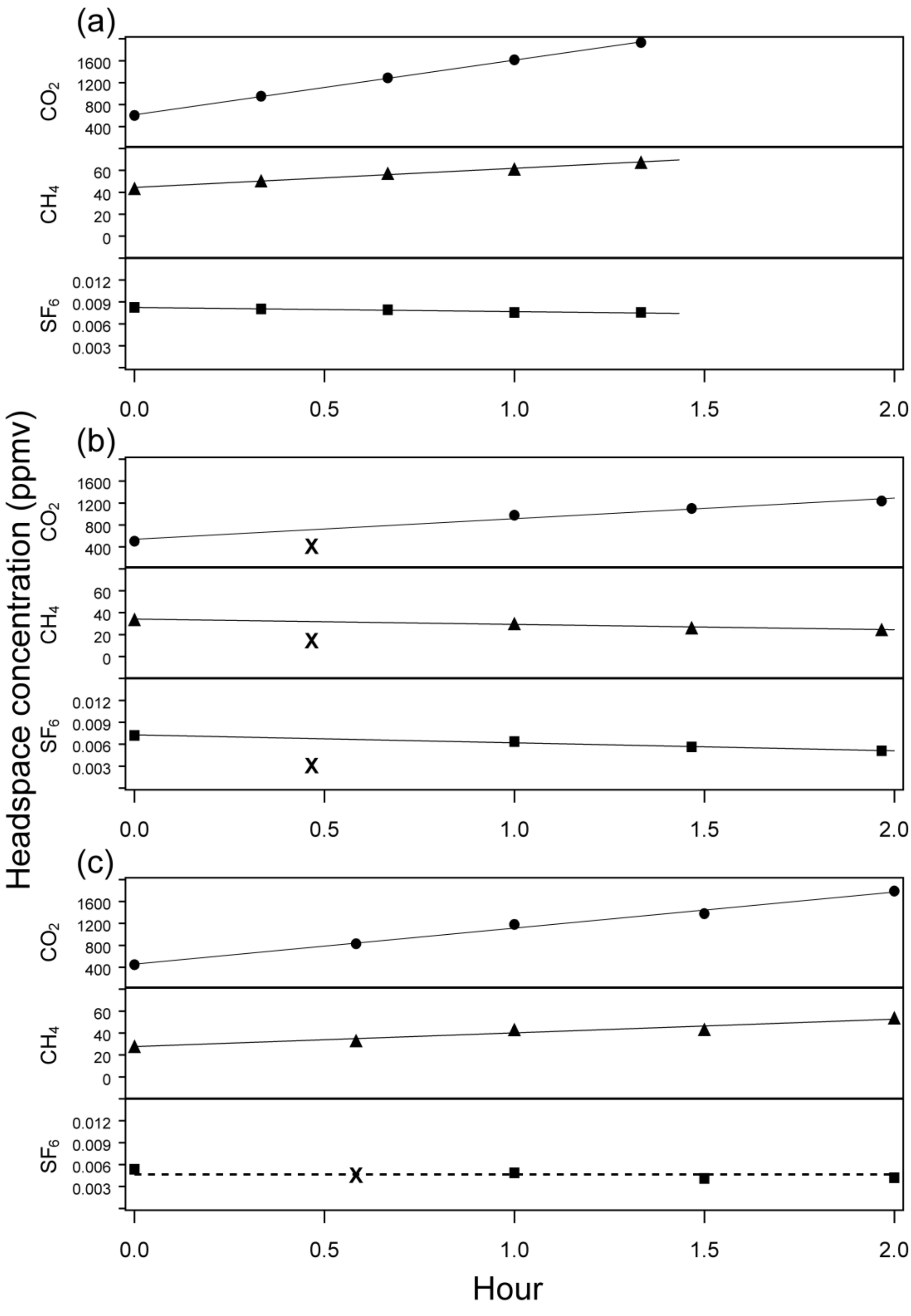

Fig. B.3 Examples of headspace concentrations of CH_4 (▲), CO_2 (●) and SF_6 (■) for three typical outcomes of the decision algorithm: (a) all gases had acceptable r^2 values (≥ 0.9, solid line); (b) after one time point was removed (**x**), r^2 values were acceptable; (c) the relationship of SF_6 against time (dashed line) was not effectively different from zero.

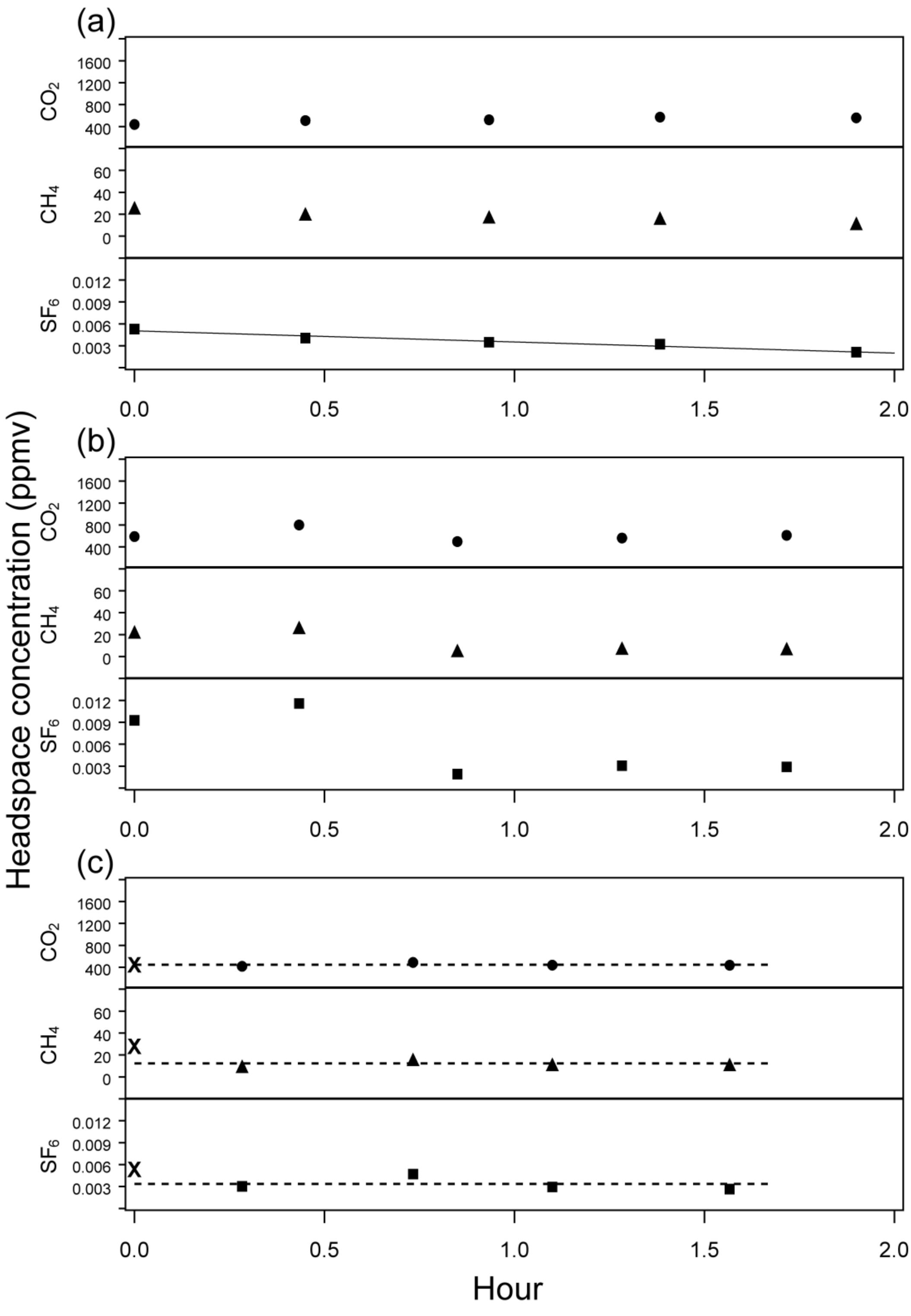

Fig. B.4 Examples of headspace concentrations of CH_4 (▲), CO_2 (●) and SF_6 (■) for three typical outcomes of the decision algorithm: (a) SF_6 decreased excessively (> 50%); (b) after one time point was removed, r^2 values were still unacceptable for all gases; (c) the relationship of all gases with time (dashed line) was not effectively different from zero.

Appendix C Data gap filling regression models

The aim of these models was to fill data gaps of more than one hour in the environmental data for three locations at the Lake Vyrnwy field site from 23 May 2008 to 31 January 2010. The fundamental approach was to correlate values across sensors at all locations in order to construct a regression model which could then be used to predict missing values. There were a number of reasons for the occurrence of data gaps including equipment failure, damage from livestock (such as chewed cables and soil temperature probes), equipment theft, water-damaged loggers and wind-damaged anemometers. Out of a potential of 445,680 hourly values across all sensors, 134 data gaps resulted in 119,372 (26.8%) missing values.

A regression model was generated for each data gap, with non-missing values used as explanatory variables in a stepwise selection procedure (PROC REG procedure with the SELECTION=STEPWISE option on SAS®, v9.2, SAS Institute Inc., Cary, NC, USA). This automated selection procedure was based on a forward step-wise regression (see page 220 of Grafen and Hails, 2002) but included a step which, once an additional explanatory variable had been added to the model, removed any existing explanatory variables in the model if their p-value increased above 0.05. All variables were categorised into five groups: soil temperature, air temperature, radiation (solar radiation and PAR), humidity, and rainfall, and each model only included independent variables from the same group as the dependent variable. In order to realistically fit night-time radiation levels and rainfall on dry days, the intercept for models of radiation and rainfall was forced through zero. All models were required to meet several criteria: the presence of at least one independent variable, produced from a similar sensor type, for the entire gap and the r^2 for the correlation between actual and predicted values had to be more than 0.8. Details of missing periods of data and the resulting gap-filling models (Table C.1 to Table C.6) and comparisons between predicted and actual values (Fig. 3.1 and Fig. C.1) show that each regression model met these criteria. The models which were constructed to fill gaps in the hourly measurements of wind speed and rainfall yielded low r^2 values (between 0.557 and 0.681), so gaps in the wind speed and rainfall data were modelled using daily values (daily total wind run and daily total rainfall). Regression models derived in this way produced acceptable r^2 values between 0.850 and 0.944 and the comparison between results from the hourly and daily approaches are shown in Table C.5 and Table C.6.

Table C.1 Periods of missing soil temperature data for various locations and vegetation types (Loc), with details of individual data gap-filling models created from stepwise regression against non-missing soil temperatures from other locations and vegetation types. Each soil temperature sensor is represented by a four letter code, where the first two characters define location (Eu = Eunant, Ha = Hafod and Hi = Hirddu) and the last two characters define type of vegetation (Gr = grass, He = heather, Ju = Juncus and Se = sedge). The coefficient of determination (r^2) and degrees of freedom (df) are given.

Loc	Missing dates	Model parameters	r^2	df
EuGr	04/10/08 - 04/03/09	EuGr = -0.422 + 0.339*HiGr + 0.065*EuHe + 1.096*EuSe - 0.452*HiSe	0.991	7105
EuGr	22/09/09 - 31/01/10	EuGr = -0.815 + 1.067*EuJu	0.953	815
HaGr	23/05/08 - 22/03/09	HaGr = 1.795 + 0.167*HiGr - 0.113*EuHe + 0.755*EuSe	0.985	1896
HaGr	03/04/09 - 01/07/09	HaGr = 1.378 + 1.053*EuGr - 0.270*EuHe + 0.205*HaHe - 0.473*EuSe + 0.318*HiSe	0.996	443
HaGr	04/07/09 - 23/09/09	HaGr = 1.666 + 0.547*HaHe + 0.332*HiHe	0.989	4962
HaGr	21/10/09 - 09/12/09	HaGr = -0.705 + 1.110*EuJu	0.980	4729
HiGr	31/07/09 - 11/08/09[1]	HiGr = 0.708 + 0.607*EuGr - 0.313*HaHe + 1.050*HiHe - 0.183*HaJu - 0.159*HiJu - 0.126*EuSe + 0.133*HaSe	0.996	1361
HiGr	11/08/09 - 21/10/09	HiGr = 0.473 + 0.43*HaHe + 0.574*HaJu	0.945	6953
HiGr	21/10/09 - 19/11/09	HiGr = -0.421 + 0.955*EuJu	0.986	3257
EuHe	22/09/09 - 19/11/09	EuHe = -2.549 + 1.152*EuJu	0.989	5154
HaHe	13/01/09 - 17/02/09	HaHe = -0.015 + 0.182*HiGr + 0.794*EuHe - 0.093*HiJu + 0.111*EuSe + 0.052*HiSe	0.997	6775
HaHe	24/02/09 - 27/02/09	HaHe = 0.075 + 0.141*HiGr + 0.793*EuHe - 0.065*HiHe - 0.095*HiJu + 0.249*HiSe	0.997	5548
HaHe	21/10/09 - 19/11/09	HaHe = -2.927 + 1.277*EuJu	0.982	5850
HaHe	27/01/10 - 27/01/10	HaHe = -0.367 + 0.090*HaGr - 0.203*HiGr + 0.659*EuHe - 0.462*HiHe - 0.147*EuJu + 0.089*HaJu + 0.158*HiJu - 0.096*EuSe + 0.472*HaSe + 0.466*HiSe	0.994	1231
HiHe	05/08/08 - 08/10/08	HiHe = -0.128 + 0.436*HiGr + 0.117*EuHe - 0.369*EuSe + 0.806*HiSe	0.993	10115
HiHe	14/01/09 - 30/01/09	HiHe = -0.284 + 0.395*HiGr + 0.230*EuHe + 0.055*HiJu - 0.434*EuSe + 0.757*HiSe	0.995	6099
HiHe	17/02/09 - 17/02/09	HiHe = -0.284 + 0.395*HiGr + 0.230*EuHe + 0.055*HiJu - 0.434*EuSe + 0.757*HiSe	0.995	6099
HiHe	04/03/09 - 07/03/09	HiHe = 0.330 + 0.049*EuGr + 0.510*HiGr + 0.100*EuHe + 0.094*HaHe - 0.301*EuSe + 0.486*HiSe	0.995	2891
HiHe	29/04/09 - 29/04/09	HiHe = 0.160 + 0.524*HiGr + 0.315*EuHe + 0.073*HaHe + 0.034*HaJu + 0.094*HiJu - 0.206*EuSe - 0.069*HaSe + 0.203*HiSe	0.998	1360
HiHe	20/10/09 - 19/11/09	HiHe = -1.981 + 1.134*EuJu	0.969	6029
EuJu	23/05/08 - 19/08/09	EuJu = 2.171 + 0.745*EuHe + 0.116*EuSe	0.989	4011

[1] This single time period included 11 periods of missing data, all of which were gap-filled using the same model.

Table C.1 continued.

Var	Missing dates	Model parameters	r^2	df
HaJu	23/05/08 - 05/06/08	HaJu = 2.197 - 0.203*HiGr + 0.501*EuHe + 0.075*EuSe + 0.046*EuGr + 0.020*HaHe + 0.283*HiHe	0.983	3194
HaJu	23/09/08 - 22/03/09	HaJu = 1.473 + 0.556*EuHe - 0.168*EuSe + 0.544*HiSe	0.991	5820
HaJu	30/04/09 - 09/07/09	HaJu = 2.161 + 0.150*EuGr - 0.236*HiGr + 0.552*EuHe + 0.146*HaHe + 0.172*HiHe - 0.164*EuSe + 0.280*HiSe	0.984	3191
HaJu	21/10/09 - 21/10/09	HaJu = -1.009 + 1.116*EuJu	0.975	5815
HaJu	01/11/09 - 09/12/09	HaJu = -1.009 + 1.116*EuJu	0.975	5815
HiJu	27/05/08 - 24/07/08	HiJu = 2.227 - 0.298*HiGr - 0.865*EuHe + 1.670*EuSe + 0.112*EuGr + 0.159*HiHe	0.984	2892
HiJu	28/08/08 - 29/08/08	HiJu = 1.779 - 0.362*HiGr - 0.818*EuHe + 1.091*EuSe + 0.533*HiSe + 0.220*EuGr + 0.146*HaJu	0.983	2808
HiJu	23/09/08 - 17/12/08	HiJu = 2.770 - 0.453*EuHe - 0.544*HaHe + 1.617*EuSe + 0.129*HiSe	0.976	6776
HiJu	15/04/09 - 29/04/09	HiJu = 1.563 - 0.135*EuGr - 0.446*HiGr - 0.753*EuHe + 0.321*HaHe + 0.472*HiHe + 0.688*EuSe + 0.395*HaSe + 0.310*HiSe	0.990	1360
HiJu	23/05/09 - 02/07/09	HiJu = 2.217 + 0.380*EuGr - 0.323*HiGr - 0.702*EuHe - 0.152*HaHe + 1.148*EuSe + 0.426*HiSe	0.985	2891
HiJu	24/07/09 - 25/07/09	HiJu = 1.563 - 0.135*EuGr - 0.446*HiGr - 0.753*EuHe + 0.321*HaHe + 0.472*HiHe + 0.688*EuSe + 0.395*HaSe + 0.310*HiSe	0.990	1360
HiJu	07/09/09 - 10/09/09	HiJu = 0.755 + 0.596*EuHe - 0.672*HaHe - 0.471*HiHe - 0.125*EuJu + 0.931*HaJu + 0.702*EuSe	0.936	735
HiJu	06/10/09 - 19/11/09	HiJu = 0.724 + 0.951*EuJu	0.984	5220
EuSe	22/09/09 - 19/11/09	EuSe = -2.835 + 1.224*EuJu	0.985	4013
EuSe	10/12/09 - 27/01/10	EuSe = -1.296 + 0.504*HaGr - 0.379*HiGr + 0.946*EuHe - 0.359*HaHe - 1.336*HiHe + 0.374*EuJu + 0.095*HaJu + 0.694*HaSe + 0.450*HiSe	0.981	1232
HaSe	29/05/08 - 22/03/09	HaSe = 0.232 + 0.264*HiGr - 0.158*EuHe + 0.843*EuSe	0.991	3741
HaSe	15/05/09 - 01/07/09	HaSe = -0.179 + 0.342*EuGr + 0.150*HiGr - 0.088*EuHe + 0.418*HaHe - 0.261*HiHe + 0.457*EuSe	0.992	2473
HaSe	19/08/09 - 23/09/09	HaSe = 0.579 + 0.618*HaHe + 0.588*HiHe - 0.243*HaJu	0.987	6239
HaSe	10/10/09 - 10/10/09	HaSe = 0.035 + 0.371*HaGr + 0.318*HaHe + 0.477*HiHe + 0.039*EuJu - 0.219*HaJu	0.997	4146
HaSe	21/10/09 - 09/12/09	HaSe = -1.941 + 1.168*EuJu	0.976	4174
HiSe	04/06/08 - 05/06/08	HiSe = -0.119 - 0.081*HiGr + 0.925*EuSe - 0.439*EuGr + 0.153*HaHe + 0.491*HiHe	0.991	5588
HiSe	31/07/09 - 11/08/09[2]	HiSe = -0.001 - 0.401*EuGr - 0.230*EuHe + 0.108*HaHe + 0.357*HiHe + 0.057*HaJu + 0.105*HiJu + 1.267*EuSe - 0.259*HaSe	0.997	1360
HiSe	11/08/09 - 21/10/09	HiSe = -0.795 + 0.472*HaHe + 0.613*HaJu	0.993	6952
HiSe	21/10/09 - 19/11/09	HiSe = -2.568 + 1.217*EuJu	0.984	3257

[2] This single time period includes 11 periods of missing data, all of which are gap-filled using the same model.

Table C.2 Periods of missing air temperature data for various locations (Loc), with details of individual data gap-filling models created from stepwise regression against non-missing air temperatures from other locations. Each air temperature sensor is represented by a two letter code which defines location (Eu = Eunant, Ha = Hafod and Hi = Hirddu). The coefficient of determination (r^2) and degrees of freedom (df) are given.

Loc	Missing dates	Model parameters	r^2	df
Eu	08/07/08 - 22/09/09	Eu = -0.535 + 1.071*Ha	0.956	10071
Eu	22/09/09 - 31/01/10	Eu = 0.129 + 1.089*Hi	0.957	8746
Ha	07/10/08 - 08/10/08	Ha = 0.825 + 0.893*Eu	0.956	10071
Ha	21/10/09 - 31/01/10	Ha = 0.629 + 0.993*Hi	0.993	11249
Hi	23/05/08 - 24/06/08	Hi = -0.552 + 0.041*Eu + 0.946*Ha	0.994	8744
Hi	10/08/08 - 11/08/08	Hi = -0.577 + 1.001*Ha	0.993	11249
Hi	23/09/08 - 08/10/08	Hi = 0.191 + 0.879*Eu	0.957	8745

Table C.3 Periods of missing PAR (Par) and solar radiation (Rad) data for various locations (Loc), with details of individual data gap-filling models created from stepwise regression against non-missing radiation measurements from other locations. Each radiation sensor is represented by a five letter code, where the first two characters define location (Eu = Eunant, Ha = Hafod and Hi = Hirddu) and the last three characters define type of measurement (Par or Rad). The coefficient of determination (r^2) and degrees of freedom (df) are given.

Loc	Missing dates	Model parameters	r^2	df
EuPar	23/05/08 - 07/10/08	EuPar = 0.002*HaRad	0.806	5977
EuPar	07/10/08 - 08/10/08	EuPar = 0.003*EuRad	0.837	5977
EuPar	08/10/08 - 28/01/09[3]	EuPar = 0.002*EuRad + 0.001*HiRad	0.843	5976
EuPar	22/09/09 - 31/01/10	EuPar = 0.068*HiPar + 0.002*HiRad	0.825	3503
HaPar	23/05/08 - 07/10/08	HaPar = 0.002*HaRad	0.863	5826
HaPar	07/10/08 - 08/10/08	HaPar = 0.003*EuRad	0.791	5134
HaPar	08/10/08 - 17/02/09	HaPar = -0.001*EuRad + 0.002*HaRad + 0.001*HiRad	0.866	5132
HaPar	24/02/09 - 27/02/09	HaPar = 0.251*EuPar - 0.001*EuRad + 0.002*HaRad + 0.001*HiRad	0.874	5130
HaPar	21/10/09 - 31/01/10	HaPar = 0.082*HiPar + 0.002*HiRad	0.852	4196
HiPar	23/05/08 - 07/10/08	HiPar = 0.002*HaRad	0.845	4197
HiPar	07/10/08 - 08/10/08	HiPar = 0.003*EuRad	0.823	3505
HiPar	08/10/08 - 29/04/09	HiPar = 0.0002*EuRad + 0.002*HiRad	0.869	3504
EuRad	23/05/08 - 22/09/08	EuRad = 0.822*HaRad	0.923	8739
EuRad	22/09/09 - 31/01/10	EuRad = 13.939*HiPar + 0.873*HiRad	0.936	3504
HaRad	07/10/08 - 08/10/08	HaRad = 1.123*EuRad	0.923	8739
HaRad	21/10/09 - 31/01/10	HaRad = 1.092*HiRad	0.970	4197
HiRad	23/05/08 - 12/08/08[4]	HiRad = 0.884*HaRad	0.949	11233
HiRad	23/09/08 - 08/10/08	HiRad = 1.031*EuRad	0.933	8402

[3] This single time period included four periods of missing data, all of which were gap-filled using the same model.
[4] This single time period included six periods of missing data, all of which were gap-filled using the same model.

Table C.4 Periods of missing humidity data for various locations (Loc), with details of individual data gap-filling models created from stepwise regression against non-missing humidites from other locations. Each humidity sensor is represented by a two letter code which defines location (Eu = Eunant, Ha = Hafod and Hi = Hirddu). The coefficient of determination (r^2) and degrees of freedom (df) are given.

Loc	Missing dates	Model parameters	r^2	df
Eu	03/08/08 - 06/08/08[5]	Eu = 4.409 + 0.954*Hi	0.930	9422
Eu	06/08/08 - 22/09/08	Eu = 9.121 + 0.917*Ha	0.906	10748
Eu	22/09/09 - 31/01/10	Eu = 4.409 + 0.954*Hi	0.930	9422
Ha	07/10/08 - 08/11/08	Ha = -0.483 + 0.988*Eu	0.906	10748
Ha	21/10/09 - 31/01/10	Ha = -2.411 + 1.010*Hi	0.960	11249
Hi	23/05/08 - 24/06/08	Hi = 2.384 + 0.355*Eu + 0.630*Ha	0.974	9421
Hi	10/08/08 - 11/08/08	Hi = 5.990 + 0.951*Ha	0.960	11249
Hi	23/09/08 - 08/10/08	Hi = 2.191 + 0.976*Eu	0.930	9422

[5] This single time period included five periods of missing data, all of which were gap-filled using the same model.

Table C.5 Periods of missing wind speed data for various locations (Loc), with details of individual data gap-filling models created from stepwise regression against non-missing wind speed data from other locations using both hourly measurements and daily wind run. Each rainfall sensor is represented by a two letter code which defines location (Eu = Eunant, Ha = Hafod and Hi = Hirddu). The coefficient of determination (r^2) and degrees of freedom (df) are given.

Loc	**Missing dates**	**Hourly wind speed**			**Daily wind run**		
		Model parameters	**r^2**	**df**	**Model parameters**	**r^2**	**df**
Eu	07/08/08 - 21/09/08	Eu = 1.770*Ha	0.776	4157	Eu = 1.842*Ha	0.881	120
Eu	22/12/08 - 31/01/10	n/a[6]			Eu = 1.596*Hi	0.863	120
Ha	22/10/09 - 31/01/10	n/a[1]			Ha = 0.878*Hi	0.986	470
Hi	23/05/08 - 23/06/08	Hi = 0.025*Eu + 1.064*Ha	0.964	2830	Hi = 1.130*Ha	0.979	120
Hi	24/09/08 - 07/10/08	Hi = 0.483*Eu	0.767	2831	Hi = 1.130*Ha	0.979	120

[6] No independent variables were present for the entire data gap.

Table C.6 Periods of missing rainfall data for various locations (Loc), with details of individual data gap-filling models created from stepwise regression against non-missing rainfall from other locations using both hourly and daily rainfall totals. Each rainfall sensor is represented by a two letter code which defines location (Eu = Eunant, Ha = Hafod and Hi = Hirddu). The coefficient of determination (r^2) and degrees of freedom (df) are given.

Loc	Missing dates	Hourly rainfall total			Daily rainfall total		
		Model parameters	**r^2**	**df**	**Model parameters**	**r^2**	**df**
Eu	07/08/08 - 21/09/08	n/a[7]			Eu = 1.131*Hi	0.850	261
Eu	23/09/09 - 31/01/10	Eu = 0.920*Hi	0.555	6217	Eu = 1.131*Hi	0.850	261
Ha	04/08/08 – 21/09/08	n/a[1]			Ha = 0.874*Hi	0.944	285
Ha	22/09/08 - 18/02/09	n/a[1]			Ha = 0.683*Eu	0.844	297
Ha	22/10/09 - 31/01/10	Ha = 0.875*Hi	0.841	6822	Ha = 0.874*Hi	0.944	285
Hi	23/05/08 – 23/06/08	Hi = 0.152*Eu + 0.818*Ha	0.849	6129	Hi = 0.239*Eu + 0.786*Ha	0.953	255
Hi	24/09/08 - 18/02/09	Hi = 0.607*Eu	0.555	6217	Hi = 0.752*Eu	0.850	261

[7] No independent variables were present for the entire data gap.

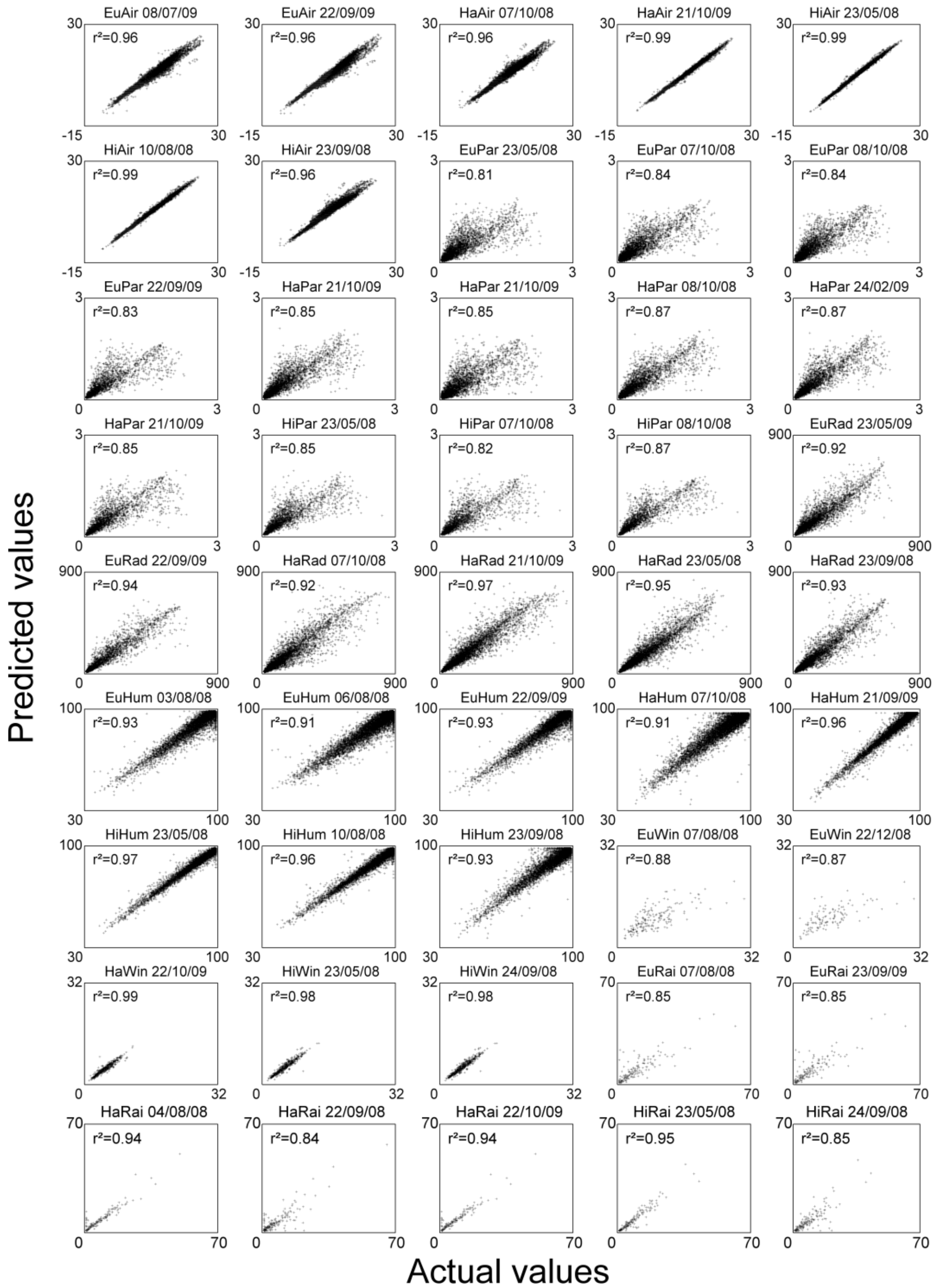

Fig. C.1 Results from data gap-filling models for each period of missing air temperature (Air, °C), PAR (Par, mmol m^{-2} s^{-1}), solar radiation (Rad, Wm^{-2}), humidity (Hum, %), wind speed (Win, ms^{-1}) and rainfall (Rai, mm) data. Each model is represented by a five letter code; the first two characters define location and the last three characters define type of measurement (Air, Par, Rad, Hum or Rai), and the starting date of the data gap.

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