Methane emissions variability from a Welsh patterned raised bog
Stamp, Imelda

The copyright of this thesis rests with the author and no quotation from it or information derived from it may be published without the prior written consent of the author

For additional information about this publication click this link.
http://qmro.qmul.ac.uk/jspui/handle/123456789/1284

Information about this research object was correct at the time of download; we occasionally make corrections to records, please therefore check the published record when citing. For more information contact scholarlycommunications@qmul.ac.uk
Methane emissions variability from a Welsh patterned raised bog

Imelda Stamp


School of Geography, 
Queen Mary, University of London, 
327 Mile End Road, 
London E1 4NS 
United Kingdom
Abstract

This work investigated the variability of CH\textsubscript{4} emissions from a Welsh raised bog – Cors Fochno – and evaluated the role of ebullition as a mechanism of CH\textsubscript{4} flux to the atmosphere.

Between 31\textsuperscript{st} March 2008 and 20\textsuperscript{th} March 2009, CH\textsubscript{4} fluxes were measured weekly/biweekly from four microform-types - mud-bottomed hollow, hummock, sedge lawn and Sphagnum lawn. CH\textsubscript{4} fluxes (measured using flux-chambers) ranged from -8.9 – 190.1 mg m\textsuperscript{-2} d\textsuperscript{-1} (n = 505). The abundance of two key species – Rhynchospora alba and Sphagnum moss - was most relevant for describing spatial variation in annual CH\textsubscript{4} emissions (best fit model $r^2 = 0.68$, $p < 0.001$). A combination of air temperature, rainfall, barometric pressure and solar radiation variables produced the best fit model of temporal variation of CH\textsubscript{4} flux ($r^2 = 0.29$, $p < 0.001$). Winter emissions represented 9.4% of the annual CH\textsubscript{4} budget of the peat dome.

CH\textsubscript{4} ebullition fluxes to 28 funnel-traps were measured weekly between 28\textsuperscript{th} May and 12\textsuperscript{th} September 2009. Daily averaged rates of CH\textsubscript{4} ebullition ranged from -1.0 – 784.5 mg CH\textsubscript{4} m\textsuperscript{-2} d\textsuperscript{-1} (n = 414). Based on assumed rates of methanotrophic processing, CH\textsubscript{4} ebullition flux to the water table was entirely consumed before reaching the atmosphere in only one week of the season. In the remaining 15 weeks it was estimated that between 5% and 81% of CH\textsubscript{4} ebullition would have escaped to the atmosphere. Ebulition was shown to be an important transport mechanism of CH\textsubscript{4} flux from Cors Fochno during the season, accounting for an estimated 7 – 36% of CH\textsubscript{4} emissions. Large changes in barometric pressure appeared to be important drivers of ebullition in some microforms. However, air temperature was the most widely-important predictor of temporal variation of ebullition fluxes during the season and during two low pressure events.
Table of Contents

Chapter 1  Introduction ........................................................................................................... 8
Chapter 2  Literature Review ............................................................................................... 11
  2.1   Methane production and consumption in peat .......................................................... 11
          2.1.1  Production ........................................................................................................ 11
          2.1.2  Oxidation .......................................................................................................... 12
  2.2   Storage of free-phase methane in peat ...................................................................... 13
  2.3   Transport pathways of methane flux to the atmosphere ......................................... 15
          2.3.1  Plant-transport & Molecular diffusion ............................................................... 15
          2.3.2  Ebullition ........................................................................................................... 17
  2.4   Spatial variability of methane emissions within patterned peatlands ................. 19
          2.4.1  Measuring small-scale variations in CH4 emissions ....................................... 19
          2.4.2  Controls on spatial variations of CH4 emissions ............................................. 20
  2.5   Temporal variability of methane emissions .............................................................. 25
          2.5.1  Abiotic controls on temporal variability of CH4 fluxes ................................... 25
Chapter 3  Methodology ....................................................................................................... 30
  3.1   Site description ............................................................................................................ 30
  3.2   Measuring CH4 emissions using flux-chambers ......................................................... 33
          3.2.1  Flux-chamber design at Cors Fochno ................................................................. 34
          3.2.2  Spatial distribution of collars ............................................................................ 36
          3.2.3  Taking flux-chamber measurements ................................................................ 37
          3.2.4  Testing for an observer effect .......................................................................... 38
          3.2.5  Measuring peat temperature and water table position .................................... 38
          3.2.6  Measuring plant species abundance ................................................................ 39
          3.2.7  Meteorological data ......................................................................................... 39
  3.3   Measuring ebullition using funnel-traps ................................................................... 40
          3.3.1  Testing the funnel-traps .................................................................................... 42
          3.3.2  Spatial distribution and installation of funnel-traps ....................................... 42
          3.3.3  Measuring ebullition fluxes to the water table ............................................... 43
  3.4   Laboratory methods ................................................................................................... 43
          3.4.1  Analysis of CH4 concentrations using the MCDA ........................................... 43
          3.4.2  New MCDA method: Syringe-injection mode ................................................. 44
          3.4.3  Testing the use of disposable syringes for sample storage ............................. 50
          3.4.4  Analysis of CH4 concentrations using gas chromatography ........................ 51
  3.5   Data manipulations and calculations ....................................................................... 52
          3.5.1  Calculating CH4 fluxes to the atmosphere ....................................................... 52
          3.5.2  Calculating funnel-gas volume at the time of measurement ......................... 53
          3.5.3  Calculating ebullition fluxes to the water table .............................................. 54
          3.5.4  Scaling-up using high-resolution aerial photographs ..................................... 56
Chapter 4  Methane fluxes from microforms of a patterned raised bog .......................... 58
  4.1   Results ........................................................................................................................ 59
          4.1.1  Seasonal CH4 fluxes .......................................................................................... 59
          4.1.2  Spatial variability of CH4 fluxes during measurement weeks ....................... 60
4.1.3 Frequency distributions of CH$_4$ fluxes from each microform-type ................................. 62
4.1.4 Comparing plant cover, water table and peat temperature between microform-types .......................................................... 63
4.1.5 Hypothesis 1 ......................................................................................................................................................... 65
4.1.6 Extrapolated CH$_4$ emissions estimate for bog dome ............................................................................. 66
4.1.7 Hypothesis 2 ......................................................................................................................................................... 68
4.1.8 Hypothesis 3 ......................................................................................................................................................... 70
4.1.9 Summary of hypothesis tests ......................................................................................................................... 72
4.2 Discussion ......................................................................................................................................................... 74
4.2.1 Comparing emissions from Cors Fochno with other patterned peatlands ................................................................. 74
4.2.2 Spatial variations of CH$_4$ emissions ........................................................................................................... 75
4.2.3 Controls on temporal variations in CH$_4$ flux .......................................................................................... 77
4.2.4 Summary of key findings ................................................................................................................................. 79
Chapter 5 Methane ebullition fluxes from mud-bottomed hollows and Sphagnum lawns ......................................................................................................................... 81
5.1 Results ......................................................................................................................................................... 82
5.1.1 Frequency distribution of bubble fluxes ................................................................................................. 82
5.1.2 CH$_4$ concentration of bubble samples ................................................................................................. 83
5.1.3 Relationship between bubble flux and CH$_4$ ebullition ......................................................................... 84
5.1.4 CH$_4$ ebullition fluxes to individual funnel-traps ................................................................................... 85
5.1.5 Hypothesis 4 ......................................................................................................................................................... 86
5.1.6 Hypothesis 5 ......................................................................................................................................................... 87
5.1.7 Seasonal CH$_4$ ebullition flux to the atmosphere ................................................................................ 90
5.2 Discussion ......................................................................................................................................................... 93
5.2.1 Size and frequency of bubble fluxes ......................................................................................................... 93
5.2.2 CH$_4$ concentration of bubble samples ................................................................................................ 94
5.2.3 Hotspots of CH$_4$ ebullition ...................................................................................................................... 95
5.2.4 Spatial variability between microform-types ........................................................................................... 95
5.2.5 Oxidation of CH$_4$ ebullition fluxes during transit between water table and atmosphere .............................................................................................................................. 96
5.2.6 Relative importance of ebullition as transport pathway for atmospheric CH$_4$ .............................................................................................................................. 97
Chapter 6 Abiotic controls on temporal variation of ebullition .............................................................................................................................. 99
6.1 Results ......................................................................................................................................................... 100
6.1.1 Variability of ebullition rates during season ............................................................................................ 100
6.1.2 Meteorological conditions during season ............................................................................................. 101
6.1.3 Low pressure events ............................................................................................................................... 104
6.1.4 Hypothesis 6 ......................................................................................................................................................... 107
6.2 Discussion ......................................................................................................................................................... 112
6.2.1 Comparing rates of ebullition ................................................................................................................ 112
6.2.2 Control of temperature .......................................................................................................................... 113
6.2.3 Control of pressure variation ................................................................................................................ 114
6.2.4 Control of wind speed .................................................................115
6.2.5 Control of rainfall .................................................................116
6.2.6 Spatially-variable response of ebullition to abiotic variables .........116

Chapter 7 Conclusions and Future research ........................................118
7.1 Overview of hypothesis test results ...............................................118
7.2 Success of research in achieving aims & objectives .......................121
  7.2.1 Measuring microform-scale emissions variation across a patterned peatland .................................................................121
  7.2.2 Quantifying ebullition fluxes to the water table and atmosphere ......122
  7.2.3 Evaluating the importance of the abiotic controls on ebullition ........123
7.3 Looking forward ...........................................................................123
  7.3.1 Improvements to future flux-chamber studies at UK peatlands ........123
  7.3.2 Evaluating the importance of methanotrophy on CH₄ ebullition .......125
  7.3.3 Investigating the link between spatial controls and temporal variations of ebullition in situ ......................................................126

Acknowledgements ............................................................................128
References ........................................................................................129
List of Figures
Figure 1: Map of north-west Ceredigion, West Wales.  .........................................................30
Figure 2: Example of a large mud-bottomed hollow microform at Cors Fochno.  ......................31
Figure 3: Elevated hummock microtopography at Cors Fochno.  ...........................................31
Figure 4: Mean monthly precipitation and mean daily maximum air temperatures for Cors Fochno, 2000 – 2009.  ..........................................................32
Figure 5: Photograph of a flux-chamber and collar used to measure CH$_4$ fluxes at Cors Fochno. ..................................................................................34
Figure 6: Schematic diagram of a flux-chamber and collar. ..........................................................35
Figures 7a & 7b: Taking flux-chamber measurements from the centre of the bog dome.  ..........................................................37
Figures 8a & 8b: Funnel-traps installed in a mud-bottomed hollow and Sphagnum lawn.  ..........41
Figure 9: Schematic diagram of a funnel-trap.  ...........................................................................41
Figure 10: Photograph of MCDA external loop modification. ....................................................45
Figure 11: Long term drift of MCDA response to 9.8 ppm CH$_4$ gas standard.  .........................48
Figure 12: Long term drift of MCDA response to 24.7 ppm CH$_4$ gas standard.  ......................49
Figure 13: Relationship between the proportion of CH$_4$ remaining in a syringe-stored gas sample and time stored.  ..........................................................51
Figure 14: Relationship between observed funnel-gas (mm) and funnel-gas volume (mL) for observations > 100 mm. ..........................................................54
Figure 15: Section of a composite orthophotograph taken during low altitude kite flights across Cors Fochno.  ..........................................................57
Figure 16: Box plot of seasonally averaged CH$_4$ fluxes for each collar. .................................60
Figure 17: Time series of within-group variability in each measurement week. ..........................61
Figure 18: Frequency distributions of CH$_4$ fluxes from each microform-type.  .......................63
Figures 19a & 19b: Boxplots of mean daily CH$_4$ flux and annual CH$_4$ emissions. ................66
Figure 20: Relationships between cover of Rhynchospora alba and annual CH$_4$ emissions and mean CH$_4$ flux from hummocks and mud-bottomed hollows. 69
Figure 21: Time-series of the most important abiotic variables driving temporal variations of CH$_4$ flux (SWR3a).  ..........................................................73
Figure 22: Frequency distributions of Sphagnum lawn and mud-bottomed hollow bubble fluxes. ..................................................................................82
Figure 23: CH$_4$ concentrations of bubble samples. .................................................................83
Figure 24: Relationships between cumulative bubble flux and CH$_4$ ebullition flux to the water table.  ...........................................................................84
Figure 25: Spatial variability of seasonal CH$_4$ ebullition fluxes to water table. ......................85
Figure 26: Box-plot of mean seasonal CH$_4$ ebullition fluxes for each microform-type.  .................86
Figure 27: Mean monthly precipitation and mean daily maximum air temperatures at Cors Caron, 2000 – 2009.  ..........................................................87
Figure 28: Box plot of average daily rates of ebullition during the season. ............................101
Figures 29a & 29b: Air temperature, rainfall, wind speed and barometric pressure during season of ebullition measurements.............................................................. 102
Figures 30a & 30b: Mean hourly rates of ebullition to water table and CH$_4$ fluxes to atmosphere during low pressure events......................................................... 105

List of Tables
Table 1: Estimates of percentage volumes of free-phase gas in peat ......................... 14
Table 2: CH$_4$ ebullition rates reported in the literature............................................. 18
Table 3: Performance comparison of established GC-FID method and new MCDM method............................................................. 50
Table 4: Summary of seasonal CH$_4$ fluxes.............................................................. 59
Table 5: Summary of CH$_4$ fluxes from each microform-type.................................. 62
Table 6: Variables used in stepwise regression models of mean daily CH$_4$ flux and annual CH$_4$ emission.............................................................. 64
Table 7: Estimated CH$_4$ emissions from bog dome .............................................. 67
Table 8: Stepwise multiple regression model of mean CH$_4$ fluxes (SWR2a)............ 68
Table 9: Stepwise multiple regression model of annual CH$_4$ emissions (SWR2b)...... 68
Table 10: Abiotic variables used in stepwise multiple regressions of CH$_4$ fluxes (SWR3a-e)........................................................................................................ 70
Table 11: Stepwise multiple regression model of CH$_4$ fluxes (SWR3a).................... 71
Table 12: Best fit multivariate partial models of CH$_4$ fluxes from each microform-type (SWR3b-e)............................................................. 72
Table 13: Comparison of climatological conditions at Cors Fochno and Cors Caron for May-September 2003 and May-September 2009........................................ 88
Table 14: Rates of potential CH$_4$ oxidation............................................................ 89
Table 15: Effect of methanotrophy on average daily rates of CH$_4$ ebullition............ 91
Table 16: Effect of methanotrophy on weekly-totalled CH$_4$ ebullition..................... 91
Table 17: Seasonal CH$_4$ ebullition to the water table and atmosphere.................... 92
Table 18: Summary of barometric pressure drops during season............................ 103
Table 19: Predictive variables used in stepwise regression models SWR6a – SWR6f. ...................................................................................................................... 107
Table 20: Stepwise multiple regression on average daily rates of ebullition during season (SWR6a).................................................................................................................. 108
Table 21: Stepwise multiple regressions for individual funnel-traps.......................... 109
Table 22: Stepwise multiple regressions on pressure event ebullition data (SWR6c & 6d)...................................................................................................................... 110
Table 23: Stepwise multiple regression on CH$_4$ flux data for pressure event 2 (SWR6f)...................................................................................................................... 110
Chapter 1 INTRODUCTION

Methane (CH₄) is an important component of the Earth's atmosphere and climate system. Atmospheric concentrations have increased from c. 715 ppb in 1750 to 1774 ppb in 2005, a rate of increase previously unseen in 650,000 years of climate history (Forster et al., 2007). Atmospheric CH₄ has a global warming potential (on a per molecule basis) 25 times greater than that of CO₂ over 100 years (Forster et al., 2007) and natural and anthropogenic CH₄ emissions have a long-term effect on climate (Solomon et al., 2007). Northern peatlands - peat-forming wetlands above 45°N - are the largest natural contributor to atmospheric CH₄ per annum, yet there are large uncertainties in how peatland CH₄ is transported to the atmosphere (Coulthard et al., 2009) and the scale of spatial variation within and between peatlands (cf. Moore et al., 1994). It is important to resolve these uncertainties if we are to improve the reliability of local, regional and global CH₄ budgets and process-based models of CH₄ exchange in peatlands. Without precise estimates of the global CH₄ budget, our understanding of the causes of increased atmospheric CH₄ and the effects on climate is limited (Mikaloff Fletcher et al., 2004).

Most northern peatlands exhibit patterning of distinct microforms (or microtopes; Ingram, 1978) ranging from shallow pools and wet depressions (e.g. mud-bottomed hollows) to dry mounds (hummocks), distinguished from one another by topography, plant species composition, microenvironment and process rates (Belyea & Clymo, 2001). This patterning has been linked to spatial variability of CH₄ emissions for some peatlands (e.g. Clymo & Pearce, 1995). However, the wider significance of patterning as a driver of emissions variability within the most globally important peatland types is unclear. Ombrotrophic (rainwater-fed) raised bogs cover a larger area than any other northern peatland type (Ingram, 1983), with the largest expanses of raised bog found in Russia (particularly Siberia) and Canada (Gorham, 1991). Raised bogs are known to be important sources of atmospheric CH₄, but few studies have investigated the spatial variability of CH₄ emissions from this important peatland type and none have thoroughly investigated the importance of ebullition (bubbling) as a mechanism of CH₄ loss. The potential importance of ebullition has been identified only relatively recently (e.g. Rosenberry et al, 2003) yet several studies now suggest that ebullition may be the most important transport mechanism for CH₄ release, particularly during falling barometric pressure (e.g. Glaser et al., 2004, Tokida et al. 2007) and in aquatic
‘hotspots’ of CH₄ flux (e.g. Pelletier et al., 2007). No study to date has quantified the frequency and magnitude of CH₄ ebullition fluxes in situ during a full summer to early autumn season (when CH₄ production rates are typically high) or provided detailed information about the distribution of terrestrial ebullition ‘hotspots’. Thus, the importance of ebullition is still unclear. Improved understanding of microform-scale variation in CH₄ fluxes and ebullition was the central aim of this research. To this end, six main hypotheses were developed for testing:

- **HYPOTHESIS 1:** At an annual scale, CH₄ emissions vary significantly between microform-types.

- **HYPOTHESIS 2:** Differences in plant cover, water table position and near-surface peat temperature explain the spatial variability of CH₄ emissions between microform-types.

- **HYPOTHESIS 3:** Air temperature, solar radiation, rainfall, wind speed, wind direction and barometric pressure are significant controls on temporal variability of daily CH₄ fluxes from each microform-type.

- **HYPOTHESIS 4:** CH₄ ebullition fluxes to the water table of mud-bottomed hollows are greater than to the water table of Sphagnum lawns.

- **HYPOTHESIS 5:** For most of the summer/early autumn season, CH₄ arriving at the water table via ebullition is oxidized before reaching the atmosphere.

- **HYPOTHESIS 6:** Air temperature, rainfall, wind speed and change in barometric pressure are important controls on ebullition. Of these, change in barometric pressure is the most important.

Justification of each hypothesis is provided by the following literature review. The review begins with an overview of current understanding of the key processes involved in the production, consumption, storage and transport of CH₄ in peat (sections 2.1 – 2.3). A review of the potential controls on spatial and temporal variability of CH₄ emissions from patterned peatland is provided thereafter in
sections 2.4 – 2.5. While the general rationale for the research is given throughout the review, where the justification of a particular hypothesis is provided, the hypothesis number is given in bold.
Chapter 2  LITERATURE REVIEW

2.1  METHANE PRODUCTION AND CONSUMPTION IN PEAT

2.1.1  PRODUCTION

CH$_4$ is produced by methanogenic Archaea which generate CH$_4$ as a metabolite of energy production (Segers et al., 1998). Methanogens are obligate anaerobes that thrive in the anoxic microsites (saturated peat pores) of near-surface peat and anaerobic peat layers below the water table. Methanogens act on simple carbon compounds (CO$_2$, acetate, methanol, methalated amines) produced during decomposition of plant material (Segers et al., 1998). Metabolically, methanogens exist as four groups, two of which produce CH$_4$ via the transfer of a methyl (CH$_3$) group from acetate, methanol and methylate amines and two which reduce CO$_2$ to CH$_4$ using H$_2$ or formate as a reductant (Edwards et al., 1998). In general, research suggests that acetate is the primary methylated compound used in peatland CH$_4$ production (e.g. Ström et al., 2003). CH$_4$ production occurs thus via two main pathways in peat: the acetoclastic reaction (CH$_3$OOH $\rightarrow$ CH$_4$ + CO$_2$) and CO$_2$ reduction (4H$_2$ + CO$_2$ $\rightarrow$ CH$_2$ + 2H$_2$O).

Acetate fermentation predominates in the acrotelm - the peat layer above the lowest water table position experienced during a dry summer (Ingram, 1978). Most CH$_4$ is produced in this zone (98% Clymo & Pearce, 1995) fuelled by the decay of young organic matter in near-surface peat (Conrad, 2005) and enhanced by the root exudation of labile organic compounds from sedges growing at the peat surface (Bellisario et al., 1999; Chanton et al., 1995; Joabsson et al., 1999; Ström et al., 2003, 2005). CH$_4$ concentration profiles have shown that CH$_4$ production varies with depth within near-surface peat (e.g. Clymo & Pearce, 1995; Strack & Mireau, 2010; Hornibrook et al., 2009). Differences in CH$_4$ production rates between microform-types have also been identified. This variation has been linked to spatial differences in thermo-hydrological regime (e.g. Saarnio et al., 1997), sedge species distribution (Ström et al., 2005), peat structure and pore water chemistry (Strack & Mireau, 2010). It may be related also to differences in decomposition processes. For example, plant litter beneath hummocks has been found to be resistant to decay (Belyea, 1996) suggesting that substrate supply to acetotrophic methanogens may be reduced in these microforms. Differences in rates of CH$_4$
production may translate into differences in CH$_4$ emissions between different microform- types (HYPOTHESIS 1).

The slow exchange of water between the acrotelm and the deeper underlying peat (the catotelm, Ingram, 1978) largely isolates deep peat methanogens from sources of acetate and other methylated compounds (Rydin & Jedlum, 2006). Deep CH$_4$ production is thus predominantly via the CO$_2$ reduction pathway (Hornibrook et al., 1996). Acetate fermentation may occur where sedge roots penetrate the upper layers of the catotelm (Ström et al., 2003) or if groundwater transports labile organic substrates downward to deeper peat layers (Hornibrook et al., 1996). The latter has been implicated in hotspots of deep CH$_4$ production and free-phase gas accumulation in the Glacial Lake Agassiz Peatland (GLAP) in Minnesota (Glaser et al., 2004) (discussed further in section 2.2). However, in general, CH$_4$ produced in the catotelm is thought to contribute little to CH$_4$ emissions from peatlands (~2% Clymo & Pearce, 1995).

2.1.2 Oxidation

A large and varying proportion of the CH$_4$ produced in peatlands is oxidized by methanotrophic bacteria before it reaches the atmosphere (20-99% Lomardi et al., 1997; Popp et al., 2000; Freznel & Karofeld, 2000; cited in Ström et al., 2005). Oxidation is performed primarily by methanotrophs, a subset of methylotrophs that use CH$_4$ as a simple-carbon compound for energy production, oxidizing CH$_4$ to methanol, formaldehyde, formate and, ultimately, CO$_2$ (Lai, 2009). Methanotrophic bacteria perform two types of oxidizing activity: Type I high affinity oxidation (at low CH$_4$ concentrations, e.g. atmospheric) and Type II low affinity (at high CH$_4$ concentrations, > 100-1000 ppmv) (Segers, 1998). Both Type I and Type II methanotrophs have been found in peat bogs and are active both above (Pearce & Clymo, 2001) and below the water table (Hornibrook et al., 2008). Typically, rates of methanotrophy are highest close to mean water table position where both substrates (CH$_4$ and O$_2$) are in abundance (Lai et al., 2009). Methanotrophs oxidise CH$_4$ using O$_2$ diffused from the atmosphere, delivered by Sphagnum mosses during photosynthesis (Frenzel & Karofeld, 2000) or transported to the rhizosphere via vascular plants (particularly sedges). As vascular plants respire, O$_2$ is transported to root and rhizome aerenchyma (internal gas-space ventilation systems) (Joabsson et al., 1999) at rates dependent on plant species (Frenzel & Karofeld, 2000) and
possibly the size of root system or oxygen-transporting efficiency (Ström et al., 2005).

Approaches to measuring the efficiency of methanotrophic processing in near-surface peat are varied and most carry significant limitations (as discussed by Clymo & Pearce, 2001). Estimates of CH$_4$ oxidation potentials for Welsh peatlands during spring and summer months have been reported recently by Hornibrook et al. (2009) based on laboratory analysis of oxidation processes in two Sphagnum peat cores and field-measurements of CH$_4$ flux and pore-water CH$_4$ concentrations at sites within intermediate fen, blanket bog, upland valley mire and raised bog. The study estimated rates of potential CH$_4$ oxidation in the range of 5 – 63 mg CH$_4$ m$^{-2}$ d$^{-1}$ (based on methanotrophic processing in 3 cm thick zones of near-surface peat) and demonstrated that low affinity methanotrophs in near-surface peat had the capacity to oxidize significantly more CH$_4$ than was delivered via diffusion from underlying peat layers (Hornibrook et al., 2009). It is possible that methanotrophs oxidize a significant proportion of CH$_4$ in gas bubbles in transit to the atmosphere. This hypothesis was not investigated by Hornibrook et al. (2009), but the potential importance of bubble-CH$_4$ oxidation has been discussed in a recent paper by Coulthard et al. (2009) and is a consideration of this thesis (HYPOTHESIS 5, discussed further in section 2.3.2).

2.2 STORAGE OF FREE-PHASE METHANE IN PEAT

Until relatively recently, CH$_4$ was assumed to exist mainly in dissolved phase below the water table. However, a growing body of evidence has demonstrated that significant amounts of free-phase gas exist in peat (see Table 1) – a significant proportion of which is gas-phase CH$_4$ (33 – 88% of total subsurface CH$_4$ stock, Tokida et al., 2005; Strack & Waddington, 2008). When the partial pressures of dissolved gases rise above the hydrostatic pressure of water, bubbles are formed (Strack et al., 2005). Hydrostatic pressure increases linearly with depth (e.g. Clymo & Bryant, 2008) thus greater dissolved concentrations of CH$_4$ are required before CH$_4$ bubbles can form in deep compared with shallow peat layers.

Where formed, CH$_4$ bubbles may become attached to peat fibres, occur within the pore spaces between them or occur within their cellular structure (e.g. within the
hyaline cells of Sphagnum moss, Waddington et al., 2009). As bubbles grow they become more likely to get stuck in pore spaces, reducing water flow and solute transfer from surrounding areas of peat (Kellner et al., 2005; cited in Waddington et al., 2009). As bubbles continue to develop, localised zones of overpressure can arise in shallow (Kellner et al., 2005) and deep peat layers (e.g. Glaser et al., 2004).

From in situ measurements the CH₄ concentration of bubbles has been shown to vary with depth within the peat profile (Strack et al., 2005; Coulthard et al., 2009; Tokida et al., 2005; Strack & Mireau, 2010). Using subsurface inverted funnel-traps in a Canadian poor fen (St. Charles-de-Bellechasse, Québec), Strack et al. (2005) measured bubble CH₄ concentrations in the range of 1.4%-83.7%CH₄ at 25 - 100 cm depths in a Sphagnum lawn, with concentrations highest in shallow peat layers. For the same peatland, Strack & Waddington (2008) later measured bubble CH₄ concentrations ranging from 28%CH₄ at 25 cm to <1% at 100 cm – averaging 10% CH₄ over the full 150 cm depth profile. In contrast to Strack et al. (2005) and Strack & Waddington (2008), on three measurement dates Tokida et al. (2005a) found that bubble CH₄ concentrations increased with depth in the near-surface peat (0-60 cm) of three lawns in the Bibai bog, Hokkaido, Japan, and bubble volumes were shown to be considerably larger at depth (60 - 100 cm) than in upper peat layers (20 – 50 cm). The exact mechanisms that control variation within the

<table>
<thead>
<tr>
<th>Study</th>
<th>Percentage volumes of free-phase gas in peat (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hanrahan, 1954; Dise, 1992</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Landva &amp; Pheeney, 1980</td>
<td>12</td>
</tr>
<tr>
<td>Hobbs, 1986</td>
<td>7.5</td>
</tr>
<tr>
<td>Brown et al., 1989</td>
<td>2 - 5</td>
</tr>
<tr>
<td>Fechner-Levy &amp; Hemon, 1996</td>
<td>8 - 15</td>
</tr>
<tr>
<td>Beckwith &amp; Baird, 2001</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Rosenberry et al., 2003</td>
<td>9 - 13</td>
</tr>
<tr>
<td>Baird et al., 2004</td>
<td>4 - 15</td>
</tr>
<tr>
<td>Kellner et al., 2004</td>
<td>~10</td>
</tr>
<tr>
<td>Comas et al., 2005</td>
<td>0 - 10</td>
</tr>
<tr>
<td>Kellner et al., 2005</td>
<td>0 - 15</td>
</tr>
<tr>
<td>Strack et al., 2005</td>
<td>5 - 15</td>
</tr>
<tr>
<td>Tokida et al., 2005</td>
<td>0 - 19</td>
</tr>
</tbody>
</table>

Table 1: Estimates of percentage volumes of free-phase gas in peat.

Taken from: Rosenberry et al., 2006
peat profile and between microform-types are unclear, but may depend on a range of factors including the locations of intense zones of \( \text{CH}_4 \) production and the physical properties of the peat matrix (Coulthard et al., 2009; Strack & Mireau, 2010).

Large accumulations of free-phase \( \text{CH}_4 \) in medium (1 - 2 m) and deep (> 2 m) peat layers have been measured in some Canadian and US peatlands using ground penetrating radar (Comas & Slater, 2007b; Strack & Waddington, 2008) or inferred from changes in peat surface elevation (e.g. Fechner-Levy & Hemond, 1996; Glaser et al., 2004) and hydraulic head (Rosenberry et al., 2003). As noted in Section 2.1, \( \text{CH}_4 \) production occurs slowly in the catotelm via the \( \text{CO}_2 \) reduction pathway, but hotspots of production via acetate fermentation may also occur. The most widely discussed evidence is that of Glaser et al. (2004) who attributed the build-up of free-phase \( \text{CH}_4 \) in deep overpressure compartments of the Red Lake Bog (GLAP, Minnesota) to a hotspot of \( \text{CH}_4 \) production (438 g m\(^{-3}\) y\(^{-1}\)) and the presence of a woody confining peat layer at c. 2 m depth. Recently, Coulthard et al. (2009) challenged the conclusion of Glaser et al. (2004) that there is sufficient supply of labile organic substrate to support hotspot production at these depths – particularly given that hydraulic gradients from overpressured compartments would preclude downward groundwater flow (Coulthard et al., 2009). More work is needed on free-phase gas dynamics in peat before the exact mechanisms that produce shallow- and deep-peat gas accumulations are fully understood.

2.3 TRANSPORT PATHWAYS OF METHANE FLUX TO THE ATMOSPHERE

2.3.1 PLANT-TRANSPORT & MOLECULAR DIFFUSION

\( \text{CH}_4 \) is lost from peat to the atmosphere via three main mechanisms: plant-transport, molecular diffusion and ebullition (Chanton, 2005). The aerenchyma of peatland vascular plants are described frequently as the most important pathway for \( \text{CH}_4 \) emissions to the atmosphere (e.g. Bellisario et al., 1999; Christensen et al., 2003b; Joabsson et al., 1999; Ström et al., 2003 & 2005). \( \text{CH}_4 \) diffusion gradients are created between peat pore-water and the aerenchyma of roots; thus providing a direct pathway for \( \text{CH}_4 \) from the peat to the atmosphere (Joabsson et al., 1999), bypassing the zone of \( \text{CH}_4 \) oxidation. Pressure gradients can arise out of temperature differences and large \( \text{CH}_4 \) concentration gradients (which influence the
total pressure of the plant system) between the interior and exterior of plants, resulting in the mass flow of CH$_4$ molecules between sites of high and low pressure – e.g. from roots to the atmosphere (Joabsson et al., 1999). Via these mechanisms, vascular plants (particularly sedges) can be responsible for a large proportion of CH$_4$ emissions from peatlands to the atmosphere (e.g. Chaser et al., 2000b; Waddington et al., 1996; Ström et al., 2005) and the distribution of CH$_4$-transporting plants can be a significant factor driving spatial variation in CH$_4$ emissions within peatlands (discussed further section 2.4.2.3).

Diffusion of CH$_4$ from peat pore-water to the atmosphere can be described (over short time intervals) by Fick’s first law:

$$ J = -D \times \left( \frac{d\phi}{dz} \right) $$  \hspace{1cm} (Eq. 1),

where $J$ is the diffusive flux of CH$_4$ (example units, mol cm$^2$ s$^{-1}$), $D$ is the diffusion coefficient for CH$_4$ in peat at a specific temperature (cm$^2$ s$^{-1}$), $d\phi$ is the difference in CH$_4$ concentration over a shallow surface peat layer (the boundary layer) (mol cm$^{-3}$) and $dz$ is the thickness of the boundary layer (cm).

Generally pore-water CH$_4$ concentrations at the bottom of the boundary layer are higher than in the atmosphere - driving a diffusive flux of CH$_4$ from the peatland to the atmosphere. Gradients change rapidly in response to fluctuations in water table position and temperature (Rosenberry et al., 2006) thus a large range of diffusive flux rates can occur. However, it is unclear how important diffusion is compared to plant transport and ebullition, particularly since diffusive fluxes can be mistaken for constant bubbling of CH$_4$ (or “steady ebullition”) (Strack et al., 2005; Strack & Waddington, 2008). For Welsh peatlands Hornibrook et al. (2009) reported that the CH$_4$ emissions via diffusion were negligible in the presence of vascular vegetation (Hornibrook et al., 2009). Strack et al. (2005) reported diffusion fluxes calculated from diffusion gradients in the range of 0.5 – 5.5 mg CH$_4$ m$^{-2}$ d$^{-1}$ for floating-peat mats at the St. Charles-de-Bellechasse poor fen (Québec). However, fluxes calculated from flux-chamber measurements often exceeded 1000 mg CH$_4$ m$^{-2}$ d$^{-1}$, suggesting to Strack et al. (2005) that high emissions were steady ebullition rather than diffusion. In a later study at the same peatland, Strack & Waddington (2008) also concluded that steady ebullition was
occurring based on observations of diffusive fluxes that were often higher than potential diffusive fluxes determined from concentration gradients.

2.3.2 **Ebullition**

Ebullition of CH$_4$ to the atmosphere occurs when the buoyant force of CH$_4$-containing gas bubbles overcomes the force that holds them in the peat (particularly surface-tension of the gas-water interface) (Coulthard et al., 2009; Waddington et al., 2009). Recent peatland studies suggest that ebullition losses can be steady and continuous, episodic or cyclical in nature (Baird et al., 2004; Comas & Slater, 2007; Glaser et al., 2004; Tokida et al., 2005b & 2007). Streams of small gas bubbles may be steadily lost to the atmosphere from near-surface peat and/or larger volumes may be emitted as a result of ‘triggers’ such as atmospheric pressure changes (e.g. Comas & Slater 2007b; Tokida et al. 2005b, 2007) and the re-opening of conduits (Glaser et al., 2004), increases in peat temperature (Fechner-Levy & Hemond, 1996) or as a result of zones of overpressure exceeding their pressure threshold (Strack et al., 2005). The relative importance of ebullition as a transport mechanism is unclear. However, several authors have demonstrated that rates of CH$_4$ ebullition to the atmosphere can exceed rates of plant-mediated transport and diffusion by several orders of magnitude (e.g. Baird et al., 2004; Glaser et al., 2004; Tokida et al., 2007).

Various techniques have been used to measure ebullition (see Table 2). Inverted funnels (funnel-traps) have been used in several studies to capture ebullition fluxes from pools and ponds (Roulet et al., 1992; Pelletier et al., 2007; Frenzel & Karofeld, 2000), at depths within peat (Strack et al., 2005; Coulthard et al., 2009) and at the water table of saturated hollows (Strack & Waddington, 2008). Funnel-traps provide a continual record of bubble fluxes and are an effective tool for measuring temporal variations of ebullition flux. Most in situ funnel-trap studies to date have not evaluated spatial variations of ebullition per se (e.g. Strack & Waddington (2008) used only two funnel-traps in 2004 and six in 2005). Spatial variation of ebullition from laboratory-incubated peat cores has been demonstrated by Baird et al. (2004) and Waddington et al. (2009) and a recent study by Mireau & Strack (2010) demonstrated potential variations of ebullition losses between ridges and hollows (discussed further in Section 2.4.2.4). One of the primary aims of this research was to provide the first evidence for both the spatial
and temporal variability of ebullition across typical terrestrial peatland microforms (HYPOTHESES 4 and 6).

Table 2: CH$_4$ ebullition rates reported in the literature.

<table>
<thead>
<tr>
<th>Study</th>
<th>Rates of ebullition (mg CH$_4$ m$^{-2}$ d$^{-1}$)</th>
<th>Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baird et al. (2004)</td>
<td>0 - 83.1</td>
<td>Laboratory cores of near-surface Sphagnum peat ($n = 8$).</td>
<td>Rates are for threshold bubble content (cf. Kellner et al., 2006) and are based on 2-4 day averages of gas collected in gas traps during 90 - 125 day incubations. No detail on barometric pressure in laboratory.</td>
</tr>
<tr>
<td>Christensen et al. (2003)</td>
<td>2.0 - 9.5</td>
<td>Laboratory cores of near-surface northern temperate/sub-Arctic peats of various compositions ($n = 4$).</td>
<td>Rates appear to be for threshold bubble content and are based on continuous measurements from throughflow chambers fixed to the cores. No detail on barometric pressure in laboratory.</td>
</tr>
<tr>
<td>Comas &amp; Slater (2007)</td>
<td>~400 - &gt;1200</td>
<td>Laboratory monolith of near-surface Sphagnum peat.</td>
<td>Rates are based on periodic measurements from chamber above monolith and include all transport mechanisms. However, bubbles were measured in the peat, and higher rates of CH$_4$ efflux seem to be associated with changes in peat bubble content.</td>
</tr>
<tr>
<td>Coulthard et al. (2009)</td>
<td>114 - 2379</td>
<td>Field measurement of gas trapped in collection funnels ($n = 9$) sunk into near surface (upper meter) peat in a marl flat.</td>
<td>Rates are daily averages based on weekly measurements of gas collected in funnel-traps over 68- days.</td>
</tr>
<tr>
<td>Glaser et al. (2004)</td>
<td>35000</td>
<td>Field measurement of (i) changes in the elevation of the surface of a Sphagnum-dominated peatland using GPS, and (ii) pressure head using piezometers installed at depths of 1, 2 and 3m</td>
<td>Rates are for short-lived (c. 4 hours) ebullition events and assume: (i) bubbles are lost from deep peat (c. 2 m), and (ii) a CH$_4$ content in the bubbles being released of 54%</td>
</tr>
<tr>
<td>Kellner et al. (2006)</td>
<td>270</td>
<td>Laboratory core of near-surface Sphagnum peat.</td>
<td>Rates are for threshold bubble content and are based on 2 - 4 day averages of gas collected in gas traps.</td>
</tr>
<tr>
<td>Pelletier et al. (2007)</td>
<td>&lt; 1 - 117</td>
<td>Field measurement of gas trapped in collection funnels on the surface of pools.</td>
<td>Rates are based on daily averages of gas measured every 10 days. Flux-chamber measurements of CH$_4$ flux (diffusion and ebullition) ranged from -32 - 8192 mg CH$_4$ m$^{-2}$ d$^{-1}$ ($n = 253$).</td>
</tr>
<tr>
<td>Rosenberry et al. (2003)</td>
<td>5000 - 11200</td>
<td>Field measurement of pressure head using piezometers installed at depths of 1, 2 and 3 m in Sphagnum peat.</td>
<td>Rates are for short-lived (hours to days) ebullition events and assume: (i) bubbles are lost from deep peat (1 - 2 m), and (ii) a CH$_4$ content in the bubbles being released of 50%</td>
</tr>
<tr>
<td>Strack et al. (2005)</td>
<td>65</td>
<td>Field measurement of gas trapped in collection funnels sunk into near surface (upper metre) peat in a Sphagnum-dominated site.</td>
<td>Rates averaged over summer season. Individual events may give figures more than an order of magnitude greater.</td>
</tr>
<tr>
<td>Tokida et al. (2005)</td>
<td>75.8 - 1232.9</td>
<td>Laboratory core of near-surface Sphagnum peat.</td>
<td>Rates are for threshold bubble content during periods of low barometric pressure and are based on high-frequency (once every 1.5 - 10 hours) measurements using a chamber fitted to the core.</td>
</tr>
<tr>
<td>Tokida et al. (2007)</td>
<td>48 - 1440</td>
<td>Field measurement from two chambers installed on a Sphagnum-dominated site.</td>
<td>Rates apply to periods of low barometric pressure and are based on high-frequency (once every 1.5 - 2 hours) measurements using the chambers.</td>
</tr>
<tr>
<td>Waddington et al. (2009)</td>
<td>1722 - 33093</td>
<td>Laboratory cores of near-surface Sphagnum peat ($n = 4$).</td>
<td>Rates are based on daily averages of gas collected in gas traps during 172 day incubations. Barometric pressures measured in laboratory every 10 min.</td>
</tr>
</tbody>
</table>

Taken from Coulthard et al. (2009) (adapted and updated).
2.4 Spatial Variability of Methane Emissions Within Patterned Peatlands

This section provides the detailed rationale for testing Hypotheses 1, 2, 4 and 5. The peat that forms under different peatland microforms varies in composition and susceptibility to decomposition (Belyea, 1996; Matson & Harris, 2006). As noted in section 2.1.1, this variation may lead to varying rates of CH$_4$ production between different microform-types and, potentially, significant differences in emissions (Hypothesis 1). Most studies which have investigated microform-scale emissions variations have been carried out on boreal peatlands in Canada and Scandinavia and mostly on areas of minerotrophic fen (e.g. Kettunen, 2000 & 2003, Pelletier et al., 2007; Saarnio et al., 1997). The work conducted by Bubier et al. (1995) was one of the first, comprehensive studies on the ecological controls on emissions variations within different peat types (bog, poor fen and rich fen in the Northern Study Area (NSA) of the Boreal Ecosystem and Atmosphere Study (BOREAS), Manitoba). Similar large-scale studies on Canadian peatland complexes examined emissions variations within areas of raised bog (e.g. Roulet et al., 1994; Bellisario et al., 1999), but to date there are no known studies that have examined the controls on microform-scale spatial variability within temperate raised bogs. Recently, spatial variability within two blanket bogs in Scotland (Auchencorth Moss, Dinsmore et al., 2009) and Ireland (Glencar peatland, Laine et al., 2007) was investigated based on year-round flux measurements. These studies demonstrate a growing awareness of the importance of understanding the controls on small-scale variations of CH$_4$ fluxes. However, it is unclear whether the controls on spatial variations in blanket bogs reflect those from raised bogs and if these CH$_4$ flux studies captured emissions variations caused by ebullition (see Section 2.4.1).

2.4.1 Measuring Small-scale Variations in CH$_4$ Emissions

CH$_4$ emissions from peatlands are often measured using flux-chamber methods. Typically, the flux-chamber method involves installing a number of collars in the field, fitting chambers to them once a week/fortnight (sometimes less frequently) and taking chamber gas samples every few minutes for c. 20 - 40 min (longer where flux rates are low, e.g. Dinsmore et al., 2007). Generally, a best fit linear regression is used to render a flux rate of CH$_4$ loss from the enclosed peat surface to the atmosphere (Coulthard et al., 2009) and where the flux is non-linear (e.g. r$^2$}
< 0.90), the flux data are discarded, assuming disturbance and/or chamber malfunction during sampling (e.g. Huttenen et al. (2003) and Pelletier et al. (2007) discarded flux measurements with an \( r^2 < 0.85 \). This approach is appropriate when measuring steady ebullition and diffusive \( \text{CH}_4 \) fluxes - most will meet the criteria for a strongly linear or ‘undisturbed’ flux. However, episodic ebullition during chamber-operation may cause the \( r^2 \) to drop well below 0.90, resulting in exclusion of ebullition flux data prior to any further analysis. Some studies have actively retained evidence of ebullition within the datasets. For example, Bubier et al. (1995) retained flux-chamber measurements “even if a large increase was observed between two of the samples as long as the correlation coefficient was still significant at \( p < 0.05 \)”. In general, however, this approach seems to be the exception and not the rule. As a consequence, it is possible the previous flux-chamber studies on emissions variations within patterned peatlands have underestimated ebullition.

2.4.2 Controls on spatial variations of \( \text{CH}_4 \) emissions

2.4.2.1 Water table position
As noted in Section 2.1.2, water table position is an important indicator of the aerobicity of surface peat layers (Bubier et al., 1995) and the potential for \( \text{CH}_4 \) oxidation (HYPOTHESIS 2). In general, average \( \text{CH}_4 \) emissions from elevated microforms such as hummocks and ridges are found to be lower than from microforms such as lawns and hollows which are positioned close to the water table (e.g. Alm et al., 1997; Clymo & Pearce, 1995; Laine et al., 2007; Pelletier et al., 2007; Waddington et al., 1996). Generally, low emissions from hummocks are attributed to high rates of \( \text{CH}_4 \) oxidation in the aerobic zone above the water table (e.g. Bubier et al., 1993; Roulet et al., 1997). However, some studies have demonstrated negligible \( \text{CH}_4 \) oxidation above the water table, with most \( \text{CH}_4 \) oxidation occurring at the boundary between the acrotelm and catotelm (e.g. Saarnio et al. 1997; Frenzel & Karofeld, 2000). Low average emissions from hummocks may also reflect reduced substrate supply for methanogenesis (caused by reduced litter input from vascular vegetation) and the increased resistance of hummock peat to decay (Saarnio et al. 1997).

Several studies have related spatially-varied \( \text{CH}_4 \) emissions to differences in water table position (e.g. Laine et al., 2007; Dinsmore et al., 2009; Alm et al., 1997; Saarnio
et al., 1997; Pelletier et al., 2007). The importance of water table position as a control on spatial variation may vary depending on the season and degree of microtopography across the study area. For example, while Laine et al. (2007) demonstrated that, overall, spatial variation in average CH$_4$ fluxes across the Glencar lowland blanket bog could be related to median water table depths (exponential regression $r^2 = .43$, $p < 0.05$), water table was a weak predictor of CH$_4$ fluxes from two types of lawn where there were small variations in topography (depths to water table ranged from 2 – 7 cm). In a 19-month investigation of microform-scale CH$_4$ fluxes at the Auchencorth Moss blanket peatland, Scotland, Dinsmore et al. (2009) could relate average CH$_4$ emissions variation to water table position in only one season (the growing season where variation in water table was at its highest). Bubier et al. (1995) demonstrated that mean water table position was a moderately strong predictor of summer-averaged emissions over a range of microform-types ($\log_{10}$ mean CH$_4$ flux, $r^2 = 0.54$, $p < 0.05$) within different peatlands of the BOREAS complex (Manitoba) while for the same peatlands Bellisario et al. (1999) found that water table position did not account for spatial variation in CH$_4$ emissions between sites where water table was consistently within 15 cm of the peat surface.

With respect to ebullition, the importance of average water table position is unclear. As noted previously in Section 2.1.2, methanotrophs in near-surface Sphagnum lawn peat can be highly efficient at processing CH$_4$ arriving from deeper peat layers via diffusion (Hornibrook et al., 2009). How well methanotrophs 'deal with' different types of ebullition is unclear and may depend on peat structure (see Section 2.4.2.4) and the speed and size of the bubble flux. Some types of episodic ebullition will be able to overwhelm or bypass the methanotrophic zone in near-surface peat (e.g. large-scale events such as those reported by Glaser et al., (2004) or short-term high flux events such as observed by Tokida et al. (2007)) while some types of CH$_4$ ebullition flux (e.g. slow, steady ebullition of small bubbles) may be partially or entirely oxidized before reaching the atmosphere (Coulthard et al., 2009). It is possible that for terrestrial peatland microforms where water table position is permanently or periodically below the peat surface (e.g. Sphagnum lawns) a significant proportion of CH$_4$ ebullition fluxes to the water table are oxidised before reaching the atmosphere (HYPOTHESIS 5).
2.4.2.2 Near-surface peat temperature

Given that rates of methanogenesis, methanotrophy and carbon turnover (controlling the labile carbon pools which provide substrate for CH₄ production) are all limited by temperature (Christensen et al., 2003) differences in near-surface peat temperature may lead to differences in CH₄ emissions between peatland microforms (HYPOTHESIS 2). For example, Bubier et al. (1995) found that differences in mean peat temperature at the water table explained two thirds of the spatial variation in summer-averaged CH₄ emissions across the BOREAS peatland complex. The microclimate and temperature regime of the near-surface peat under different peatland microforms is strongly influenced by water table position and the vegetation cover at the peat surface (Rydin & Jedlum, 2006). The lower water content of ‘dry’ hummock peat compared with ‘wet’ lawns and hollows means that the surface of hummocks warms quicker than the surface of lawns/hollows, but temperatures in the rooting zone of hummocks are kept down by the dry overlying peat (Rydin & Jedlum, 2006). For example, Frenzel & Karofeld (2000) found that peat temperatures 0 – 80 cm below the surface of hummocks in July were significantly lower than below hollows (Männikjärve bog, Endla patland complex, C. Estonia). They attributed the cooler conditions below the hummocks to thermal insulation by the dry hummock peat above. Vegetation cover and plant species composition affects rates of evaporation and albedo. Near-surface peat temperatures in ‘wet’ microforms such as lawns and hollows are kept down during the summer by high rates of evapotranspiration, which are governed largely by plants (Rydin & Jedlum, 2006). In ‘dark’ sparsely vegetated areas of bare peat (e.g. mud-bottomed hollows), albedo and rates of evapotranspiration can be expected to be lower than in microforms with high cover of relatively light-coloured vegetation (e.g. Sphagnum pulchrum lawns). As a result, surface peat temperatures may be higher in mud-bottomed hollows than vegetated lawns in summer months. Higher peat temperatures in mud-bottomed hollows may lead to higher rates of CH₄ production and bubble-CH₄ formation in these microforms, contributing to higher rates of CH₄ loss and ebullition (HYPOTHESIS 4) (see also section 2.5.1.1 for the influence of temperature on ebullition).

2.4.2.3 Vegetation cover

The density or abundance of vascular plants (particularly sedges) and gradients and groupings of other key plant species have been shown to be good predictors of spatial variations of CH₄ emissions (e.g. Bubier et al., 1995; Pelletier et al., 2007).
The distribution of sedges has been identified as an important factor controlling CH₄ emissions variability within Canadian and Scandinavian peatlands (e.g. Bellisario et al., 1999; Bubier et al., 1995; Nilsson et al., 2001; Tuittila et al., 2000; Pelletier et al. 2007) and several studies on UK and Irish peatlands have identified a link between vascular plants (sedges, rushes and Menyanthes trifoliata in particular) and sites of high CH₄ emissions (e.g. Laine et al., 2007; McNamara et al., 2008) (HYPOTHESIS 2). Using vegetation cover as a predictor of emissions enables remote sensing or high-resolution photographs to be used for scaling-up, potentially improving the reliability of the peatland-scale emissions estimate (e.g. Becker et al., 2008). In general, most studies that have used clipping experiments to investigate the role of sedges concur that sedges stimulate emissions of CH₄ (e.g. Waddington et al., 1996), with areas of a peatland containing sedges having higher CH₄ flux rates than those without (e.g. Frenzel & Karofeld, 2000; Strack et al., 2006). However, some studies have demonstrated a negative correlation between the abundance of sedges and CH₄ emissions (e.g. Dinsmore et al., 2009), possibly due to increased plant-mediated O₂ transport to the rhizosphere (which can inhibit methanogenesis and enhance methanotropy in and around roots (Chanton, 2005), section 2.1.2). Despite identifying sites of high emissions to correspond to hollows with particular vegetation, Laine et al. (2007) showed that CH₄ flux was not correlated with the vascular green leaf area of CH₄-transporting species. The importance of sedges as predictors of variation may depend on the types of sedge species present within the study areas (e.g. Joabsson et al., 2000; Ström et al., 2003; Ström et al., 2005) and their stage in the seasonal growth/senescence cycle (Saarnio et al., 1997; discussed further in Section 2.5.1.2).

With respect to ebullition, it is possible that the presence of vascular plants can both enhance and reduce the production and build-up of CH₄ bubbles in near-surface peat. Root exudation from vascular plants may increase rates of CH₄ production (Joabsson et al., 1999; Waddington et al., 1996; Ström et al., 2003) and bubble formation in near-surface peat. Conversely, the effect of plant-mediated O₂ diffusion could be a reduction in rates of bubble formation, growth, and loss. It is not clear which of these processes is most important with respect to bubble dynamics and ebullition.
2.4.2.4 **PEAT TYPE & STRUCTURE (EBULLITION)**

As noted previously in Section 2.1.1, differences in CH$_4$ production rates between microform-types have been linked to differences in plant litter and decay rates (Belyea, 1996), thermo-hydrological regime (e.g. Saarnio et al., 1997), sedge species distribution (Ström et al., 2005), peat structure and pore water chemistry (Strack & Mireau, 2010). Variations in the build-up and release of CH$_4$-containing gas bubbles are linked to rates of CH$_4$ production and to the ability of the peat to store bubbles and the ease with which bubbles can move upwards through the peat pore spaces (Baird et al., 2004; Coulthard et al., 2009; Kellner et al., 2006). As a result, bubble storage and ebullition may vary across a peatland due to localised differences in peat type and structure beneath microforms. Porous, loosely packed peat may be more conducive to upward bubble flux while peat with lower porosities and smaller pore networks may be more likely to trap and retain gas bubbles (Kettridge et al., 2010; in review). While these hypotheses have not been tested thoroughly in the field, novel recent work by Strack & Mireau (2010) at a large poor fen in Alberta, Canada, found that the entrapment of bubbles varied spatially between microform-types. Free-phase gas content was found to be typically higher beneath ridges (elevated features comparable to hummocks) than Sphagnum hollows/lawns. Strack & Mireau (2010) attributed this to differences in vegetation and physical properties of the peat. Ridges consisted of woody roots and densely-packed Sphagnum fuscum compared with lawns of loosely packed, porous Sphagnum angustifolium and abundant sedge roots. Higher bulk density, the presence of confining roots and smaller pore sizes enabled more free-phase gas to remain ‘trapped’ within the ridge peat than the Sphagnum hollow/lawn peat (Strack & Mireau, 2010). With respect to the near-surface peat of mud-bottomed hollows and Sphagnum lawns, one might expect the sloppy, highly-decomposed mud-bottomed hollow peat (von Post H scores 8/9) to be less able to trap and retain gas bubbles than weakly/moderately-decomposed Sphagnum lawn peat (von Post H scores 3/4). As a result, rates of CH$_4$ ebullition might be expected to be higher from mud-bottomed hollows than from Sphagnum lawns due to the relative ease with which bubbles can move vertically to the water table (HYPOTHESIS 5).
2.5 **TEMPORAL VARIABILITY OF METHANE EMISSIONS**

To understand the controls on temporal variations of CH\textsubscript{4} flux from northern peatlands and the importance of wintertime emissions, it is necessary to conduct year-round CH\textsubscript{4} flux studies on a range of peatland types. It has been demonstrated that peatlands can lose a substantial amount of CH\textsubscript{4} during the winter (e.g. Alm et al., 1999). However, most peatland CH\textsubscript{4} flux studies are conducted in spring and summer months only; producing uncertainty in annual CH\textsubscript{4} budgets for northern peatlands (Bryne et al., 2004; cited in Baird et al., 2010b). Furthermore, it has been suggested that flux data obtained during calm weather and stable pressure conditions is preferentially reported in the literature (Tokida et al., 2005b), thus the ‘true’ variability of CH\textsubscript{4} fluxes from peatlands in response to rain, wind and falling pressure may have been underestimated. The following sections report on the findings of previous work that has linked meteorological variables to CH\textsubscript{4} flux variations from peatlands and provide the rationale for investigating the importance of air temperature, solar radiation, barometric pressure, rain and wind variables in this research (**Hypotheses 3** and **6**).

2.5.1 **ABIOTIC CONTROLS ON TEMPORAL VARIABILITY OF CH\textsubscript{4} FLUXES**

2.5.1.1 **AIR TEMPERATURE**

Large seasonal variations in CH\textsubscript{4} emissions have been demonstrated from studies that have measured CH\textsubscript{4} fluxes year-round (e.g. Roulet et al., 1994; Moore et al., 1994; Saarnio et al., 1997). Seasonal variations have been linked to seasonal changes in near-surface peat temperatures (e.g. Laine et al., 2007) and the link between temperature and rates of methanogenesis, methanotrophy and substrate supply. The near-surface peat layer has the highest range of temperatures during the year (Coulthard et al., 2009) and is the most important peat layer for CH\textsubscript{4} production (e.g. Daulat and Clymo, 1998) (see Section 2.1.1). CH\textsubscript{4} production is related exponentially to temperature (Dunfield et al., 1993) and, in general, the literature suggests that that CH\textsubscript{4} production is more temperature-dependent than CH\textsubscript{4} oxidation (e.g. Dunfield et al., 1993; Segers, 1998). As a result, CH\textsubscript{4} emissions can be expected to increase with temperature, provided transport processes are not inhibited. Temperature also affects rates of plant growth and the phenology of peatland plants (Saarnio et al., 1997), both of which can affect the supply of fresh litter and root exudates to methanogens at different times during the year.
(discussed further in Section 2.5.1.2). As a result of these interacting factors, CH$_4$ emissions might be expected to be highest during summer and lowest in winter (e.g. Alm et al., 1999; Laine et al., 2007). Although relatively low, winter emissions can make a significant proportion of the annual CH$_4$ budget, due to the persistence of CH$_4$ produced during summer in peat pore-waters and continued CH$_4$ production (albeit at slower rates). Between 2 and 22% of total annual CH$_4$ release have been reported to occur during the winter in temperate (Melloh & Crill, 1996) and boreal peatlands (Dise, 1992, cited in Alm et al., 1999). For the Glencar blanket bog, Laine et al. (2007) showed that the proportion of the annual CH$_4$ flux emitted during winter/spring (November – April) varied between 10 – 31% depending on microform-type.

With respect to ebullition, there are no known studies that have quantified ebullition flux variation during the year and little is known about how much of the seasonal variation in CH$_4$ emissions can be related to changes in ebullition rates. In the laboratory, increasing temperatures has been shown to enhance ebullition due to increased rates of CH$_4$ production and pore-water CH$_4$ concentrations (Kellner et al., 2006; Waddington et al., 2009). Increasing temperatures can also enhance ebullition due to bubble expansion (and increased buoyancy) (Ideal Gas Law) and the formation of new bubbles (or growth of existing bubbles) as gases come out of solution (Henry's Law) (Fechner-Levy & Hemond, 1996; Strack et al., 2005). Conversely, decreasing temperatures might be expected to reduce ebullition due to a reduction in CH$_4$ production rates and increased gas solubility, resulting in the transfer of CH$_4$ from the gaseous to dissolved phase (Strack et al., 2005). As a result, it might be expected that CH$_4$ ebullition would be higher in summer than in relatively cool autumn and winter months.

2.5.1.2 SOLAR RADIATION

One of the primary controls on CH$_4$ production is the amount of high-quality organic material from fresh plant litter/root decay and root exudation (Matson & Harris, 2006). Several studies have observed that CH$_4$ emissions from peatlands and other wetland types are positively correlated with net ecosystem productivity (NEP), suggesting a link between high input of fresh substrates and stimulation of CH$_4$ production (Whiting & Chanton, 1993; Chanton et al., 1995; Waddington et al., 1996). The supply of plant litter and root exudates for methanogenesis may show seasonal variation due to seasonality in rates of photosynthesis and the
growth/senescence cycle of vascular plants (Saarnio et al., 1997) in response to changes in air temperature and solar radiation (HYPOTHESIS 3). During the growing season, most of the carbon fixed by peatland vascular plants is allocated to below-ground tissues (Joabsson et al., 1999; Ström et al., 2003). Increasing carbon assimilation by vascular plants during the growing season implies that more labile carbon is being allocated to roots and that there is greater potential for both rhizospheric CH$_4$ production (Joabsson et al., 1999; Hornibrook et al., 1997) and plant-transport of CH$_4$ to the atmosphere (Waddington et al., 1996). Ström et al. (2003) demonstrated that the amount of labile carbon found in the root vicinity of two peatland sedges – Eriophorum scheuchzeri Hoppe. and Dupontia psilosantha (Rupr.) Hult. - was partially dependent on rates of photosynthesis. Plant leaves reduce their rates of photosynthesis and begin to senesce when reductions in day length and solar radiation or other environmental cues signal the onset of winter. Reductions in photosynthesis and senescence of the above-ground parts of vascular vegetation may contribute to the low CH$_4$ flux rates observed in winter (Alm et al., 1999).

2.5.1.3 BARMETRIC PRESSURE

Several recent studies have shown that drops in barometric pressure can ‘trigger’ episodic ebullition (Section 2.3.2, Table 2). Falling barometric pressure and increasing temperature can enhance ebullition by (i) increasing the volume occupied by existing bubbles and (ii) causing new bubbles to form as gases come out of solution (HYPOTHESIS 6). The Ideal Gas Law defines how bubbles expand and contract in response to pressure and temperature changes while Henry’s Law defines how pressure and temperature affect the solubility of dissolved CH$_4$ in peat pore-water. When the Ideal Gas Law and Henry’s Law are combined and differentiated with respect to pressure (Eq 2) and temperature (Eq 3), the effect of each abiotic factor (with the other held constant) on bubble formation and expansion in peat are defined as follows:

$$\frac{dv_g}{dp} = \frac{v_g}{P} - \frac{v_{pw}RT}{PH}$$  \hspace{1cm} \text{(Eq. 2)},$$

and

$$\frac{dv_g}{dT} = \frac{v_g}{T} + \frac{v_{pw}RT}{HRT^2} \times \frac{dHRT}{dT}$$  \hspace{1cm} \text{(Eq. 3)},$$
where $V_g$ is the volume of bubble gas ($m^3$), $V_{pw}$ is the volume of peat pore water in which $V_g$ resides ($m^3$), $P$ is the absolute pressure of the bubble (assumed to be the sum total of hydrostatic pressure and atmospheric pressure) (Pa), $T$ is the temperature of the bubble (K), $H$ is the dimensionless Henry’s Law constant and $R$ is the universal gas constant ($J$ mol$^{-1}$ K$^{-1}$) (Fechner-Levy & Hemond, 1996; Kellner et al., 2006; Waddington et al., 2009). Not all drops in barometric pressure lead to ebullition losses (e.g. Rosenberry et al., 2003; Kellner et al., 2006; Strack et al., 2005; Comas & Slater, 2007; Waddington et al., 2009). The effect of pressure may vary according to peat type and may not be present in some peat types (e.g. Waddington et al., 2009). Kellner et al. (2006) demonstrated that temperature, pressure and a constant CH$_4$ production term (based on a production rate of $\sim$15 µg CH$_4$ g$^{-1}$ d$^{-1}$) provided the best fit model of temporal variation of ebullition from near-surface Sphagnum peat cores ($r^2 = 0.66$, c. 100-day period). By the authors’ own admission, the model needed to be improved (e.g. to allow for CH$_4$ production term to vary over time) and it has not been tested in the field. However, the evidence from the Kellner et al. (2006) study illustrates the need to treat the temporal variability of ebullition as a multivariate problem – affected by abiotic factors that control rates of methanogenesis, bubble formation, expansion and buoyancy (HYPOTHESIS 6).

2.5.1.4 Rainfall and Wind
Rainstorm events have been reported to cause episodic fluxes of CH$_4$ (Ketunnen et al., 1996) and temporarily suppress CH$_4$ emissions (Frolking & Crill, 1994). Rainfall events can affect rates of microbial methanogenesis and methanotrophy by introducing competing electron acceptors such O$_2$, NO$_3^-$ and SO$_4^{2-}$ and diluting concentrations of dissolved gases (Kettunen et al., 1996) (cited in Hornibrook et al., 2009) (HYPOTHESIS 3). Rainfall also affects emissions through its influence on water table fluctuations. In patterned peatlands, water table position generally oscillates around the mean for most of the year ($\pm2$-3 cm, Clymo & Pearce, 1995). Zones of methanogenesis and methanotrophy are thought to follow these fluctuations closely (Rydim & Jedlum, 2006), and some populations of methanotrophs may become active when water tables are lowered (Edwards et al., 1998). A lowering of the water table may also result in poisoning of methanogenic populations with O$_2$ and increased competition from aerobic microorganisms for the methylated carbon compounds used in methanogenesis (Segers, 1998). Water
table drawdown may also affect rates of plant-mediated transport of CH$_4$ and CH$_4$ production from root exudates. When a greater proportion of the roots of vascular plants are exposed to aerobic conditions, fewer roots are able to provide substrate to methanogens and transport CH$_4$ from below the water table (Waddington et al., 1996). Several studies have reported enhanced CH$_4$ emissions via ebullition in response to water table drawdown (Glaser et al., 2004; Moore et al., 1990; Rosenberry et al., 2003; Strack et al., 2004, Treat et al., 2007). Reductions in hydrostatic pressure caused by low rainfall can mobilize entrapped gas bubbles and enhance the flux of bubbles to the water table (HYPOTHESIS 6). Ebullition in response to water table drawdown was thought to explain the positive relationships between water table position and individual and monthly-averaged CH$_4$ fluxes observed by Treat et al. (2007) in a multiyear study of CH$_4$ emissions from Sallie’s Fen, New Hampshire (USA).

It is possible also that wind speed is an important control on ebullition rates from peatlands. Wind is caused by air pressure gradients which accelerate the movement of air from areas of high to low pressure. Given the influence of pressure on bubbles in peat (Section 2.5.1.3), short-lived air pressure changes may trigger short bursts of CH$_4$ ebullition from peat to the atmosphere and wind speeds or wind ‘gustiness’ may correlate with rates of ebullition over short time periods (HYPOTHESIS 6). It is possible also that strong winds agitate bubbles trapped around Sphagnum fibres and vascular plant roots and rhizomes in near-surface peat, enhancing ebullition fluxes of CH$_4$ to the atmosphere. The influence of wind on ebullition has not been tested in the field or laboratory. Thus, the importance of wind to CH$_4$ flux variations is as yet unknown.
Chapter 3  METHODOLOGY

To test HYPOTHESES 1, 2 and 3, CH₄ emissions to the atmosphere from four types of microform were measured over a full year using flux-chambers. To test HYPOTHESES 4, 5 and 6, ebullition fluxes to the water table of 28 microforms were measured during summer and early autumn using funnel-traps. In addition, to test HYPOTHESIS 6 CH₄ fluxes (chambers) and ebullition fluxes (funnel-traps) were measured at high-resolution during the passages of two low pressure systems. This chapter presents the methods and calculations used to derive rates of CH₄ flux and ebullition from field-based measurements and laboratory analysis of gas samples. Statistical analyses used to test each of the hypotheses are described in CHAPTERS 4, 5 and 6. HYPOTHESES 1, 2 and 3 are assessed within Chapter 4 “Methane fluxes from microforms of a raised patterned bog”, HYPOTHESES 4 and 5 in Chapter 5 “Methane ebullition fluxes from mud-bottomed hollows and Sphagnum lawns” and HYPOTHESIS 6 in Chapter 6 “Abiotic controls on temporal variation of ebullition”.

3.1  SITE DESCRIPTION

CH₄ flux and ebullition measurements were taken between 31st March 2008 and 12th September 2009 at Cors Fochno, an ombrotrophic raised bog approximately 10 km north of Aberystwyth in Ceredigion, West Wales (52°30′ N, 04°1′ W) (Figure 1).

Figure 1: Map of north-west Ceredigion, West Wales.
Cors Fochno is the largest estuarine expanse of primary, undisturbed raised bog within the UK and is considered to be one of only a few sites in the UK that is representative of typical northern peatland (Harris et al., 2006; Kettridge & Binley, 2008). The peatland complex is classified as a Special Area of Conservation and forms part of the Dyfi Estuary Biosphere Reserve. This research was conducted at Cors Fochno due to the near-natural condition of the central bog dome, the availability of auxiliary hydrological and meteorological data, and the typical patterns of microforms (hummocks, lawns and mud-bottomed hollows) across the bog dome (see Figures 2 and 3).

Figure 2: An example of a large mud-bottomed hollow microform at Cors Fochno.

Figure 3: Elevated hummock microtopography at Cors Fochno.
Common plant species across the bog dome include the Sphagnum mosses - Sphagnum pulchrum (Lindb.) Warnst., Sphagnum cuspidatum Ehrh., Sphagnum capillifolium (Ehrh.) Hedw., Sphagnum fuscum (Schimp.) Klinggr., Sphagnum papillosum (Lindb.) and Sphagnum magellanicum Brid. and vascular plants including the sedges Common and Hare’s Tail Cotton-grasses (Eriophorum angustifolium Honck. and Eriophorum vaginatum L.) and White-beaked Sedge (Rhynchospora alba (L.) Vahl) and the heaths Calluna vulgaris (L.) Hull and Erica tetralix L.. Other common plant species are Bog Asphodel (Narthecium ossifragum (L.) Huds.), Bog Rosemary (Andromeda polifolia L.), Bog Myrtle (Myrica gale L.); Bogbean (Menyanthes trifoliata L.), Round-leaved Sundew (Drosera rotundifolia L.) and Greater Sundew (Drosera anglica Huds.).

The centre of the bog dome reaches an elevation of c. 5.5 m above sea level (a.s.l.) while the peripheral areas of the peatland complex are c. 3.5 m a.s.l. (Mike Bailey (Site Manager), pers. comm). Mean annual temperature at Cors Fochno is c. 9.9 °C and annual precipitation is c. 1220 mm yr⁻¹ (Fron-dirion Meteorological Office Met. station, Tal-y-bont, 2000 - 2009). Seasonality of precipitation and maximum daily air temperatures at the site are shown in Figure 4.

Figure 4: Mean monthly precipitation and mean daily maximum air temperatures for Cors Fochno (Fron-dirion Met. Station, Tal-y-bont, 2000 - 2009). Bars and points represent the monthly means while error bars represent the standard deviation.
3.2 MEASURING \( \text{CH}_4 \) EMISSIONS USING FLUX-CHAMBERS

\( \text{CH}_4 \) emissions from peatlands are typically measured using either eddy covariance or flux-chamber methods. The former are more suited to measurements of \( \text{CH}_4 \) emissions at the landscape scale. Vertical wind speeds and gas concentrations are measured from instruments mounted on flux towers. Problems with the application of the method include (i) difficulties measuring vertical wind speeds and gas concentrations simultaneously, (ii) limitations of the technology for measuring some gases accurately at very high frequencies, (iii) changes in wind speed and direction, altering the footprint of the measurements and (iv) difficulties in measuring emissions from small areas of interest (e.g. particular areas of a peatland) (Denmead, 2008; Baird et al., 2010a). Flux-chambers are more suited to \( \text{CH}_4 \) flux measurements at small spatial scales. Flux-chambers comprise two main components - a removable lid (the chamber) and static frame (collar) inserted into the peat. When the chamber and collar are sealed (i.e. the flux-chamber is operational), a volume of air is isolated at the peat surface and a \( \text{CH}_4 \) exchange rate between the peat and atmosphere can be calculated from the change in \( \text{CH}_4 \) concentration in the air over time. ‘Dynamic closed’ flux-chambers generally comprise an open-path circulation system coupled to an on-line gas sensor, such as a laser spectroscopy instrument (e.g. Christensen et al, 2003b; Mastepanov et al., 2008), that detects real-time \( \text{CH}_4 \) concentration changes within the enclosed air. A constant flow of ‘sweeper-gas’ (external gas of optimal \( \text{CH}_4 \) composition) through the circulation system allows a steady-state \( \text{CH}_4 \) concentration gradient to be maintained across the enclosed peat-atmosphere boundary, minimising perturbations to natural rates of diffusion. Dynamic chambers are often automated, enabling high-frequency measurements of \( \text{CH}_4 \) flux over extended periods of time. However, they are expensive to deploy in the field, can operate only with adequate power supply and, because of these problems, there is a limit to the spatial replication of flux-measurements across large areas (even where multiplexer arrangements are employed, e.g. Mastepanov et al., 2008). In contrast, ‘static closed’ flux-chambers are simple in design, inexpensive to build and operate and can be deployed widely. The observer seals the chamber to the collar and headspace samples are collected, by hand, at regular intervals for analysis off-line (i.e. in a laboratory). Unlike with automated dynamic chambers, high frequency measurements are difficult to maintain with manually-operated static chambers. However, measurements can be replicated over large areas. For this reason, static
Closed chambers were used at Cors Fochno so that CH₄ fluxes could be measured over a large area of the bog dome (see Section 3.2.2).

3.2.1 Flux-chamber design at Cors Fochno

For both dynamic and static closed flux-chambers, important design considerations include: construction materials; enclosure geometry; minimizing perturbations to barometric air pressure, air and peat temperature during operation; gas-tightness of the chamber-collar seal; and, for closed chambers, promoting mixing of the enclosed air (Denmead, 2008). At Cors Fochno, the chambers and collars were constructed from plastics that were inert with respect to CH₄. Chambers were purchased from a specialist aquarium distributor (Aquatics Online), each constructed from rigid, translucent, 6 mm thick acrylic plastic (see Figures 5 and 6). To allow flux measurements to be taken from microforms containing large Calluna vulgaris plants, chambers were 22.6 × 25.7 × 47.4 cm (width × height × length) and had basal areas and volumes of 0.11 m² and 0.028 m³, respectively.

Figure 5: Photograph of a flux-chamber and collar used to measure CH₄ fluxes at Cors Fochno.
Four holes were drilled into the top of each chamber to insert: (i) a 14 mm self-sealing rubber septa (Fisher Scientific) to enable direct sampling using syringes; (ii) a balloon to compensate for pressure changes in the chamber upon removal of headspace samples and transmit external pressure changes into the chamber; (iii) a probe to measure temperature, humidity and barometric pressure (Commeter C4141) fitted to a 31 mm base-diameter rubber stopper (Fisher Scientific); and (iv) a 1.5 m length of Tygon tubing (3.2 mm inner diameter (i.d.), 6.4 mm outer diameter (o.d.)) to allow headspace sampling from c. 2 m distance (from 1st August 2008, shown in Figure 7b section 3.2.3). The Commeter C4141 Thermometer-Hygrometer-Barometer probe had a manufacturer's stated accuracy of ± 0.4 °C, ± 0.01 kPa. Each chamber was fitted with a removable, reflective cover (reflective fibre-reinforced foil) to minimise solar-warming of enclosed air and potential disturbance to rates of gas flux (the cover is removed in Figure 5). A fan was attached to the chamber interior and operated during sampling to encourage mixing of the enclosed air. Chambers were tested in the laboratory for gas-tightness before the onset of flux measurements in March 2008. Thereafter, field-based checks and maintenance were carried out regularly throughout the year.

Twenty collars (22.6 × 10 cm (width × height) in cross-section) were constructed from 4 mm thickness polyvinylchloride (PVC) to fit the basal area of the chamber (0.11 m²). Methods for achieving a gas-tight union between chamber and collar include foam gaskets held in place with clamps, air-tight overlaps or abutting
joints (Matson & Harriss, 1995), foam tape (Turetsky et al., 2008) and water-filled gutters around the edge of the collar (e.g. Pelletier et al., 2008; Tokida et al., 2007). At Cors Fochno, the latter method was used because it provided a gas-tight seal while causing minimal disturbance to the peat during chamber placement. Each collar was fitted with a gutter made from lengths of cable trunking (25 ×16 mm in cross-section) and sealed using aquarium-grade sealant (Dow Corning).

3.2.2 Spatial distribution of collars

As noted in Chapter 2, one of the main aims of the research was to investigate spatial variability of CH₄ emissions between different types of microform (HYPOTHESES 1 and 2). Four broad classifications of microform-type were identified within the bog dome via multiple site-walkovers in November 2007 and January 2008. Along a hydrological gradient (wettest to driest): (i) mud-bottomed hollows with water table at or above the peat surface and sparsely vegetated with Sphagnum cuspidatum, Menyanthes trifoliata and the sedges Rhynchospora alba and Eriophorum vaginatum; (ii) Sphagnum pulchrum lawns with water table c. 2 - 4 cm below the peat surface, containing R. alba and Eriophorum spp.; (iii) Sphagnum pulchrum lawns with a water table position c. 5 – 7 cm below peat surface with a dense cover of both sedges and the vascular plants Erica tetralix and Myrica gale; and (iv) hummocks with a water table position c. 15 – 35 cm below the peat surface vegetated with the heaths Calluna vulgaris and E. tetralix and Sphagnum capillifolium. The two lawn microform-types were termed Sphagnum lawns (ii) and sedge lawns (iii), respectively. Within each broad classification there were differences in species abundance between individual microforms and, for the hummocks, differences in height and elevation above the water table. 15 individual microforms were used for the installation of 20 collars. The 15 microforms selected for flux-chamber measurements were considered to be representative examples of each microform-type. Eight were located along the central boardwalk (for ease of access and in order to minimise damage to vegetation during the course of the study) and seven were off-boardwalk in the middle of the bog dome. The collars were installed in January 2008 - five collars per microform-type.
3.2.3 TAKING FLUX-CHAMBER MEASUREMENTS

Flux-chamber measurements were taken between 31st March 2008 and 20th March 2009. During this period, measurements were taken from the collars every one or two weeks (29 measurement weeks in total) over 2-4 days in order to test HYPOTHESES 1, 2 and 3. Flux-measurements were all taken between 07:00 and 18:00 (GMT), with the timing for each collar rotated in order to minimize potential for temporal (diurnal) bias in the flux data. Where collars were not sited immediately adjacent to the central boardwalk, chambers were operated via 1 × 2 m mobile boardwalk sections (see Figure 7a). Before operating the flux-chambers, the sampling-tube was purged with ambient air and the collar gutter filled with water. After sealing the chamber, three 10 mL headspace samples were extracted into 10 mL disposable syringes (Fisher Scientific Ltd, SZR-205-092K) via the rubber septum and sealed with silicone stoppers. Thereafter, one 10 mL headspace sample was extracted every 5 min for 25 - 40 min either directly from the chamber (31st March to 31st July) or via the sampling-tube (shown in Figures 6 & 7b). When using the sampling-tube, the tube was purged 10 s prior to taking the headspace sample. The final samples were taken in triplicate. All headspace samples remained

Figures 7a & 7b: Taking flux-chamber measurements from the centre of the bog dome.
in the disposable syringes prior to CH$_4$ analysis using a Methane and Carbon Dioxide Analyser or MCDA (Los Gatos Research Inc. - see Section 3.4.1 for method). Pressure and temperature readings from the Commmeter probe were noted at each sampling time to enable calculation of the mass of CH$_4$ in each 10 mL sample (see Section 3.5.1). As part of the test of HYPOTHESIS 6, CH$_4$ flux measurements were taken at high- frequencies from two mud- bottomed hollows during the passages of two low pressure systems - pressure event 1 from 3$^{rd}$ – 6$^{th}$ July 2009 and pressure event 2 from 2$^{nd}$ – 4$^{th}$ September 2009. The same measurement and analysis protocols were applied as per the weekly/biweekly measurements in 2008.

3.2.4 TESTING FOR AN OBSERVER EFFECT

During flux-chamber measurements, particular care was taken to minimise disturbance to surface peat and the potential for unnatural ebullition by (i) using the central boardwalk and mobile boardwalk sections to access the collars, (ii) sampling from a distance via the sample tubing, (iii) minimising observer movement around the collars, and (iv) taking great care when fitting the chamber to the collar. To evaluate whether the observer's movement and proximity to the chamber triggered episodic ebullition, tests were carried out during August 2008 at four microforms - two accessible via the central boardwalk and two using mobile boardwalk sections. During each test, headspace samples were taken from the flux-chambers over 25 min with the observer initially seated next to the flux-chamber (sampling directly from the chamber as soon as it was sealed) and thereafter seated c. 2 m away, sampling every 5 min via the sampling-tube. The observer moved towards the flux-chamber twice during flux-chamber operation (at 6 and 16 min) and remained next to it for 2 min before returning to the 2 m sampling point. Flux rates were all strongly linear ($r^2 > 0.93$) and there was no evidence of episodic ebullition due to the observer moving or being seated next to the chamber.

3.2.5 MEASURING PEAT TEMPERATURE AND WATER TABLE POSITION

Peat temperature and water table were hypothesised to exert a significant control on CH$_4$ emissions variability across Cors Fochno (HYPOTHESIS 2). To test this hypothesis, peat temperature measurements were recorded immediately after flux-chamber use with a temperature probe inserted into the peat to 20 cm depth next to the collar and left in place for 2 min to allow the reading to stabilise. Water
table measurements were taken using 13 dipwells installed c. 60 cm from each collar during March and April 2008. Dipwells were constructed from 75-cm lengths of PVC tubing (4 cm o.d.) drilled with 1 cm holes along the full length at c. 2.5 cm intervals. Water table position was determined manually by measuring the vertical distance between the top of the dipwell and: (i) the water table, (ii) the peat surface immediately adjacent to the dipwell, and (iii) the peat surface in the centre of the area enclosed by the collar (using a 1 m spirit level that was extended from the top of the dipwell to the centre of the collar). To ensure that the water table was not artificially elevated by the weight of the observer, a mobile boardwalk was used during measurements.

3.2.6 Measuring Plant Species Abundance

To test HYPOTHESIS 2, plant species abundance within each collar was measured using high resolution (5 Mega pixel) photographs and field surveys. The collars were photographed (Casio Elixim digital camera) each month between May and December 2008. Detailed field-based surveys were conducted in August 2008 to confirm species identities. To calculate species abundance, the photographs from November 2008 were superimposed with a grid subdivided into 105 (c. 1.7 × 1.7 cm) equal squares and examined at 3× magnification. If a plant species was found to occupy any part of a grid square, its presence was recorded. The percentage cover of each plant species was calculated by dividing the number of squares it occupied within the grid by 105 (data shown in CHAPTER 4).

3.2.7 Meteorological Data

Meteorological data used in the tests of HYPOTHESES 3 and 6 were obtained from an on-site automatic weather station (AWS; Skye Instruments MiniMet) and a local Meteorological Office manual weather station (Fron-dirion, Tal-y-bont, c. 1 km SE of the southern margin of Cors Fochno). The AWS rain gauge at Cors Fochno is an Environmental Measurements Ltd ARG100 Tipping Bucket Raingauge based on a design from the Institute of Hydrology (now Centre for Ecology and Hydrology) and records every c. 0.2 mm of rainfall. Air temperature is measured with a Skye Instruments SKH 2070 RHT+ relative humidity and temperature probe (manufacturer's stated accuracy for air temperature is ± 0.2 °C for 0 - 60 °C). Incoming solar radiation is measured with a Skye Instruments SKS 1110
Pyranometer and wind direction and speed with a Vector Instruments Potentiometer Windvane W200P and a Switching Anemometer A100R. The wind vane is accurate to within ± 3° of the actual bearing. The anemometer has a threshold of 0.2 m s\(^{-1}\) and an accuracy of 1% of the reading for windspeeds between 10 and 55 m s\(^{-1}\) (2 % for higher speeds). Barometric pressure is recorded using a Van Essen BaroDiver (accuracy ± 0.1 hPa, resolution 0.1 hPa).

During the study period, the AWS datalogger recorded hourly-averages of readings taken every 30 s (for barometric pressure they were 2-hourly spot measurements). The rainfall record was interrupted between 1st January and 27th March 2009 due to a problem with the logging-device. Daily rainfall totals for this period (used in the test of HYPOTHESIS 3, CHAPTER 4) were obtained from the Fron-dirion (Tal-y-bont) Meteorological Office station, collected using a standard Meteorological Office Mk II collection gauge. In addition, there was uncertainty in the air temperature record between May and September 2009 due to a component failure. The AWS air temperature record during this period was replaced using calibrated daily air temperatures from Tal-y-bont (recorded at 09:00 GMT each day). The calibrated data were used in the test of HYPOTHESIS 6 (CHAPTER 6).

### 3.3 Measuring Ebullition Using Funnel-Traps

To test HYPOTHESES 4, 5 and 6, ebullition to the water table was measured directly using inverted funnels (see Figures 8 and 9). The basic principle of design was based on the inverted water-filled funnel-traps employed by Strack et al. (2004) in the St-Charles-de-Bellechasse poor fen (Québec). Bubbles that enter the funnel displace the water within. The change in the volume of trapped gas provides a measure of ebullition over time. Once sufficient gas has accumulated in the funnel-trap, samples can be extracted and analysed for CH\(_4\). Strack et al. (2004) used c. 10 cm diameter plastic funnels which are potentially permeable to CH\(_4\). At Cors Fochno, funnel-traps were constructed from 25 cm diameter glass funnels with a 3 mm wall (the largest commercially available at the time) so as to maximise bubble ‘catchment area’ and minimise permeation of CH\(_4\) through the funnel-trap walls. The spouts of the funnels were replaced (by a glassblower) with 3.6 × 10 cm lengths of 3-mm wall glass tubing (the measurement tube) and each funnel-trap was fitted with a 25 cm length of 1 mm graduated measuring tape (in Figure 8b only a 10 cm tape is shown). Rubber stoppers (3.5 cm base diameter) were used to
Figures 8a & 8b: Funnel-traps installed in a mud-bottomed hollow and Sphagnum lawn

Figure 9: Schematic diagram of a funnel-trap.
seal the top of the measurement tube. Each was drilled and fitted with: (i) a c. 50 cm sampling tube (Tygon, 3.2 mm (i.d.)) with 3-way valves at each end to allow funnel-gas to be sampled using disposable syringes, and (ii) a water-tube (Tygon, 6.4 mm i.d.) for use when the funnel-trap was being filled (see Section 3.3.3). Funnels were wrapped with a reflective cover so to minimise solar heating of the entrapped gas bubble and funnel-water, leaving a measurement window uncovered so that funnel-gas measurements could be taken. Tubing and valves were sealed into place using aquarium-grade sealant (Dow Corning) and tested thoroughly for gas-tightness.

3.3.1 Testing the Funnel-Traps

Prior to installation in the field, all funnels were tested for gas-tightness over 48 hr. In-field operation was replicated in a bath of water, with each inverted funnel being placed in the water, sealed with a modified stopper and evacuated, causing the bath water to fill the funnel. Where the modified stopper was not gas-tight, water table position would immediately begin to drop. If this occurred each seal (e.g. between stopper and 3-way valve or water tube) was checked, fixed and re-tested. Once installed in the field, funnels were re-tested over 48 hr and, thereafter, regularly inspected for signs of damage. Modified stoppers were found to be faulty (seals degraded) for two funnel-traps (5 and 8) and they were decommissioned for a total of two and four weeks, respectively, during the May - September study period.

3.3.2 Spatial Distribution and Installation of Funnel-Traps

Funnel-traps were installed in 14 mud-bottomed hollows and 14 Sphagnum lawns in May 2009. Each microform was representative of the microform-type and none contained collars for flux-chamber measurements. Each funnel was installed by first carefully cutting and removing a cylindrical section of surface-peat (approx. dimensions 30 cm × 10 cm (diameter × depth)). Where vascular plants were present, particular care was taken to ensure the plants were clipped rather than pulled-out; thereby minimizing the production of artificial conduits for bubble flux. Funnel-traps were installed with the measurement window facing north to minimise solar-warming during the day and then sealed with the modified rubber stoppers. Once in situ, the trapped gas within the funnel-trap was extracted using
a 100 mL gas syringe, thereby drawing water up into the funnel from the peat column or adjacent reservoir (via the water tube).

3.3.3 MEASURING EMBOLITH FLUXES TO THE WATER TABLE

To test HYPOTHESES 4, 5 and 6, funnel-gas was measured weekly between 11:00 and 12:00 (GMT). As part of the test of HYPOTHESIS 6, measurements were taken at higher frequencies (every 3 - 10 hr) during the passages of two low pressure systems. The size of the funnel-gas ‘bubble’ was measured using binoculars from c. 2 m distance so as to minimise disturbance around the funnel-traps. Measurements of funnel-gas (mm) were converted thereafter into a volume (mL) (see Section 3.5.2).

Gas samples were taken from funnel-traps on 8\textsuperscript{th} June, 4\textsuperscript{th} July, 9\textsuperscript{th} August and 13\textsuperscript{th} September. Prior to sample collection, the sampling tube was evacuated using a 20 mL disposable syringe and closed at both ends (using the 3-way valves). Thereafter, one or two 12 mL funnel-gas samples were extracted into 20 mL disposable syringes (via the 3-way valve at the end of gas sampling tube) and transferred into pre-evacuated vials (Labco Limited). The samples were subsequently analysed for CH\textsubscript{4} concentration using a gas chromatograph (see Section 3.4.4). After samples had been collected, the remainder of the gas was extracted (using the same method) and the total volume of gas recorded. The volume of any bubbles drawn from the underlying peat during this process was noted.

3.4 LABORATORY METHODS

3.4.1 ANALYSIS OF CH\textsubscript{4} CONCENTRATIONS USING THE MCDA

Unique to this study was the use of a Methane and Carbon Dioxide Analyser (MCDA) - an off-axis laser spectroscopy instrument from Los Gatos Research Ltd - for analysis of discrete, flux-chamber headspace samples. As noted in Section 3.2, CH\textsubscript{4} flux measurements can be made in ‘real time’ by connecting CH\textsubscript{4} analysers such as the MCDA to flux-chambers in the field. At Cors Fochno, the lack of power supply and infrastructure to support on-line analysis necessitated that gas samples be collected for analysis off-site. Sending samples back to the laboratory for analysis would have placed severe financial and time constraints on the study,
particularly given the high number of samples analysed during the year (> 6000) and weekly/biweekly sampling regime. Instead, the concentration of CH$_4$ in each headspace sample taken from the flux-chambers was analysed using the MCDA which did not require laboratory facilities and was based close to Cors Fochno for the duration of the study. Out-of-the-box, the MCDA was configured only to support flow-through analysis (i.e. direct connection to a flux-chamber); thus, a modification was developed to enable syringe-stored samples of headspace gas to be analysed.

3.4.2 NEW MCDA METHOD: SYRINGE-INJECTION MODE

The author of this thesis modified the instrument, established the operating protocols and conducted all tests on the new MCDA method. The calculations given throughout this section were derived by Professor Andy Baird (University of Leeds), a supervisor of this thesis. The work comprising the following sections (3.4.2.1 - 3.4.2.5) has been published in Ecohydrology as:


3.4.2.1 DESIGN

The modification comprised a 50 cm$^3$ stainless steel, double-ended cylinder connected to two 12” (30.4 cm) sections of polytetrafluoroethylene (PTFE)-lined stainless steel braided hosing. One end of the hosing connects to the $\frac{1}{4}$” (6.35 mm) outlet port at the back of the instrument and the second to a 0.5 µm particulate filter attached to the $\frac{1}{4}$” (6.35 mm) inlet port (Figure 10). All components for this assembly (including reducing unions, nuts and ferrules) were purchased from Swagelok London UK (London Fluid System Technologies Ltd) and are designed for use in high-pressure applications. To facilitate injection of gas samples, a $\frac{3}{8}$” (9.5 mm) hole was drilled through the sample cylinder to which a threaded 1¼” (31.75 mm) section of copper tubing was fitted and sealed with a gas-tight 14 mm rubber septum (Fisher Scientific). All threaded connecting unions were coated with PTFE tape to ensure gas-tightness; once assembled, the loop was leak tested using a gas leak detector spray.
3.4.2.2 Operation and Calculations

To calculate CH$_4$ concentration of syringe-stored samples, gas standards of known CH$_4$ concentrations were required (for instrument calibration and other calculations) along with the temperature and barometric pressure of the room housing the MCDA. As in field measurements, a Commeter C4141 Thermometer-Hygrometer-Barometer probe (Comet Systems, Czech Republic) with a manufacturer's stated accuracy of ± 0.4 °C and ± 0.01 kPa was used. Approximately 30 min prior to operating the MCDA, all calibration gases (Helium, various CH$_4$-air mixtures) were transferred to 1 L Tedlar gas bags (purged three times, not overfilled) to allow the gas to come to room temperature and pressure.

Firstly, it was necessary to calculate the total number of moles of gas in the entire MCDA loop - external loop (Figure 10) plus internal components (MCDA measurement cell and connecting tubes). The quantity of gas occupying the MCDA loop was denoted $G_{\text{mol-MCDA}}$. To calculate $G_{\text{mol-MCDA}}$, the MCDA was switched on with one end of the external loop left unattached (so that the MCDA was in flow-through mode). After allowing ambient air to flow through the MCDA for c. 30-60 s (purging the internal components), the unattached end of the external loop was connected to the MCDA (syringe-injection mode). Once stable, the CH$_4$ concentration of the gas within the MCDA loop was noted. When expressed as a concentration – i.e. ppm CH$_4$ / $10^6$ – this new stable reading was thereafter denoted $C_o$. 

![Figure 10: Photograph of MCDA external loop modification.](image-url)
10 mL of helium (He) was then extracted from the 1 L Tedlar bag and injected into the loop (via the sample cylinder septum). Room temperature and pressure were noted; thus providing the temperature and pressure of the injected He sample.

\[ C_n = \frac{C_o \times G_{mol-MCDA}}{G_{mol-MCDA} + G_{mol-s}} \]  

(Eq. 4),

where \( C_n \) is the \( CH_4 \) concentration in the MCDA loop after the He injection, and \( G_{mol-s} \) the number of moles of gas in the sample of He (calculated from the Ideal Gas Equation). This equation was solved for \( G_{mol-MCDA} \) to give:

\[ G_{mol-MCDA} = \frac{C_o \times G_{mol-s}}{C_o - C_n} \]  

(Eq. 5).

Having established \( G_{mol-MCDA} \), it was then possible to calculate the \( CH_4 \) concentration in flux-chamber gas samples. This concentration value was thereafter denoted \( C_s \). Firstly, the MCDA loop was purged for c. 30-60 s by disconnecting the external loop from either the inlet or outlet. After purging, the external loop was reconnected and \( C_o \) noted (once the MCDA had stabilised). The flux-chamber sample was then injected into the loop for c. 2 min (or until the MCDA had stabilised) before noting the \( CH_4 \) reading displayed on the MCDA screen. When expressed as a concentration, this value was denoted \( C_n \).

To calculate the \( CH_4 \) concentration of the flux-chamber sample, Eq. 6 was then applied after solving for \( C_s \) (Eq. 7):

\[ C_s = \frac{(C_o \times G_{mol-MCDA}) + (C_s \times G_{mol-s})}{G_{mol-MCDA} + G_{mol-s}} \]  

(Eq. 6),

which, when solved for \( C_s \), gives:

\[ C_s = \frac{C_n \left( G_{mol-MCDA} + G_{mol-s} \right) - (C_o \times G_{mol-MCDA})}{G_{mol-s}} \]  

(Eq. 7).
Use of Eq. 7 required two assumptions; firstly, that the number of moles in the flux-chamber sample could be calculated. As the volume of the flux-chamber sample was known (10 mL at the time of sampling) and temperature and pressure of that sample were also known (by measuring temperature and pressure in the enclosure), then the Ideal Gas Equation could be used to calculate $G_{\text{mol-s}}$ (in the same way as for the He sample when estimating $G_{\text{mol-MCDA}}$). Secondly, it was assumed that $G_{\text{mol-MCDA}}$ would not change if the temperature and pressure in the room housing the MCDA were stable; if temperature and pressure did change, $G_{\text{mol-MCDA}}$ was recalculated using the Ideal Gas Equation.

To evaluate the precision of the estimates of $G_{\text{mol-MCDA}}$, tests were conducted over several months of ‘typical’ MCDA operation. At the start of each 2-8 h day of flux-chamber gas analysis, a 1 L Tedlar gas bag was purged three times, filled with 99.999% He (Scientific and Technical Gases UK), and then left to equilibrate to room temperature for 30 min. Five 10 mL syringe samples of He were then injected into the MCDA loop over 45 min, with the loop being opened and purged before each injection. Room temperature and pressure were measured each time the MCDA loop was closed prior to injection. By applying Eq 4b, five $G_{\text{mol-MCDA}}$ values were thus derived for each operating date. To evaluate the precision of estimating $G_{\text{mol-MCDA}}$ values on 19 dates were analysed where room temperature and pressure remained stable during MCDA analysis of at least three of the five He injections. The coefficient of variation (% relative standard deviation or %RSD) was used to compare variability in $G_{\text{mol-MCDA}}$ values across the 19 dates; %RSD values ranged from 0.17-4.45, with a mean of 2.33. This variability contributes a small source of error to the calculated $\text{CH}_4$ concentration of the analysed sample – $C_s$. For example, sensitivity analysis on a $C_s$ value of 3.000 ppm $\text{CH}_4$ (from date 17 where the maximum %RSD of 4.45 was observed) produced an associated error of only ±0.064 ppm; using a mean $G_{\text{mol-MCDA}}$ value of 0.013257104 mol and standard deviation of ±0.000511568 mol.

3.4.2.3 METHOD ACCURACY & LONG TERM DRIFT

The accuracy of the new MCDA method was assessed by analysing the response of the MCDA to injections of three external standards of $\text{CH}_4$ (4.9, 9.8 and 24.7 ppm). The standards were supplied by Scientific and Technical Gases UK with a quoted accuracy of 1%. After calculating $G_{\text{mol-MCDA}}$ via analysis of He injections (method described previously), four 1-L Tedlar gas bags were purged, filled with each of the
standards and left to equilibrate to room temperature for 30 min. Five 10 mL repeat injections of each gas standard were then analysed using the new method. Instrument response was plotted against gas standard concentration and a linear regression line fitted through the data. This provided an initial calibration curve for the MCDA in syringe-injection mode. Thereafter, five repeat injections of each of the four standards were re-run every 13-19 days over a 70 day period.

For each test date, very good linear calibration relationships ($r^2 > 0.99$) were found between the MCDA output and the standard gases; good precision was also found (0.78-1.76 %RSD, where precision was calculated for the repeat injections). Drift in the instrument response was assessed via trend (regression) analysis of all test data over the 70 day period (with all test data being first referenced to the initial calibration equation). No instrument drift was detected in the 4.9 ppm gas standard data ($p > 0.05$). However, both the 9.8 and 24.7 ppm standards revealed evidence of drift ($p < 0.05$). A regression line fitted through all the 9.8 ppm data suggested a general linear drift over the 70 days ($r^2 = 0.70$) (Figure 11). However, no difference was observed between days 1 and 13 nor between days 32, 42 and

![Figure 11: Long term drift of MCDA response to 9.8 ppm CH₄ gas standard.](image)

69. A non-linear trend ($p < 0.05$ when the independent variable – elapsed time in days – was $\log_{10}$-transformed) was detected in the 24.7 ppm concentration data (Figure 12). Averaged instrument response to the 9.8 and 24.7 ppm standards during the course of the 70-day period (based on five repeat injections on days
1 and 69) decreased by 9.8% and 11.5% respectively. These drifts suggested it was important to re-calibrate the modified instrument regularly (at the start of every measurement week).

Figure 12: Long term drift of MCDA response to 24.7 ppm CH₄ gas standard.

3.4.2.4 SHORT-TERM DRIFT

Instrument stability over a typical day of operation (2-8 hr) was assessed by analysis of repeat injections of the 2.6 ppm (1% accuracy) CH₄ gas standard. Following five replicate He injections to derive G⁺mol-MCDA, three 10 mL samples of 2.6 ppmv gas standard were injected into the MCDA loop. Thereafter, a single 10 mL sample of the gas standard was injected every eighth flux-chamber sample during the course of the operational day. This pattern of testing was repeated on eight operational days within a four week period. Regression analysis was used to evaluate drift in instrument response during the course of each operational day. No trend in the data was identified on six of the eight days (p > 0.05). On operational days 3 and 7 there was evidence of drift (p < 0.05) over 3 hr 40 min and 6 hr of operation, respectively, with a linear downward trend on day 3 and an upward non-linear trend on day 7. However, despite these trends, values only changed from a maximum of 2.72 to a minimum of 2.57 ppm on day 3 and from a minimum of 2.56 ppm to a maximum of 2.65 ppm on day 7. In general, therefore, the new method appeared to give stable responses during the course of a typical analysis session.
3.4.2.5 **Comparison of GC-FID and MCDA Syringe-Injection Techniques**

To assess how the MCDA loop method compared with an established GC-FID technique (see Section 3.4.4 for details), precision of the two methods was compared via repeat analysis of external gas standards (2.6, 4.9, 9.8 and 24.7 ppm \( \text{CH}_4 \)). For GC-FID analysis, five 10 mL samples of each gas standard were injected into 12 mL pre-evacuated vials (Labco Limited) using a gas-tight syringe. Analysis was performed by five repeat injections of each of the four external standards. MCDA analysis was performed by five repeat injections of the same standards. Results indicated very good precision for the new MCDA method at all concentrations (see Table 3) with substantially better precision for lower concentration standards (2.6 and 4.9 ppm) than the GC-FID method. Good precision for all standards demonstrates the high sensitivity of the MCDA in syringe-injection mode, confirming its suitability for field-based (non-laboratory) use; that is, confirming its suitability as an alternative for GC-FID techniques.

<table>
<thead>
<tr>
<th>( \text{CH}_4 ) Standard (ppm)</th>
<th>Precision of GC-FID method</th>
<th>Precision of MCDA loop method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Std. Dev. (^a) (ppm)</td>
<td>RSD (^a) (%)</td>
</tr>
<tr>
<td>2.6</td>
<td>0.225</td>
<td>7.17</td>
</tr>
<tr>
<td>4.9</td>
<td>0.144</td>
<td>2.37</td>
</tr>
<tr>
<td>9.8</td>
<td>0.075</td>
<td>0.71</td>
</tr>
<tr>
<td>24.7</td>
<td>0.239</td>
<td>0.98</td>
</tr>
</tbody>
</table>

\(^a\) based on five repeat injections

### 3.4.3 **Testing the Use of Disposable Syringes for Sample Storage**

All flux-chamber headspace samples were analysed using the MCDA within 96 hr of being collected/sealed in the disposable syringes (95% were analysed within 72 hr). The syringes were medical grade (used for liquids and gases), but there was potential for sample-degradation between headspace sampling and analysis due to the permeability of the plastic with respect to \( \text{CH}_4 \). To correct for \( \text{CH}_4 \) loss over time, a linear relation \((r^2 = 0.91)\) between the proportion of \( \text{CH}_4 \) in the syringes and time stored was established using the four \( \text{CH}_4 \) gas standards (2.6, 4.9, 9.6 and 24.7 ppm) stored in the syringes for 0 - 96 hr (see Figure 13). Three samples of each
standard were extracted into disposable syringes and sealed with silicone stoppers (as in the field). The three control samples of each gas standard were analysed immediately for \( \text{CH}_4 \) using the new MCDA method and, thereafter, three samples from each standard were analysed after 24, 48, 72 and 96 hr. The linear regression equation shown in Figure 13 was used to adjust the \( \text{CH}_4 \) concentration of each headspace sample based on the time that the sample had been stored.

![Figure 13: Relationship between the proportion of \( \text{CH}_4 \) remaining in a syringe-stored gas sample and time stored.](image)

3.4.4 **Analysis of \( \text{CH}_4 \) Concentrations Using Gas Chromatography**

\( \text{CH}_4 \) analysis of bubbles captured in the funnel-traps was carried out using a gas chromatograph (GC - Agilent 7890A) equipped with a flame ionised detector (FID) and Gerstel MPS 2 Twister autosampler. The carrier gas was zero grade \( \text{N}_2 \) at a flow rate of 25 mL min\(^{-1}\). Zero grade \( \text{H}_2 \) (30 mL min\(^{-1}\)) and air (moisture and hydrocarbon-free; 400 mL min\(^{-1}\)) were the auxiliary gases used to run the FID, operated at 155°C. The chromatographic column was a 6 ft (1.83 m) Poropak Q with 80/100 mesh heated to 40°C. Peaks were detected and integrated using Agilent’s Chemstation software (Rev B.03.01). All funnel-gas samples remained stored in 12 mL pre-evacuated vials prior to GC-FID analysis. The storage period ranged from 1 - 8 weeks. The precision of the GC-FID method with respect to four external gas standards has been shown previously in Table 3.
3.5 DATA MANIPULATIONS AND CALCULATIONS

3.5.1 CALCULATING CH₄ FLUXES TO THE ATMOSPHERE

To calculate a flux rate (in units of mg CH₄ m⁻² d⁻¹) from each flux-chamber measurement the following were required: (i) the volume of the flux-chamber (volume of chamber + collar above the peat surface, ~33.1 L); (ii) the temperature (Tᵢ) and pressure (Pᵢ) of the enclosed air (as noted at the time of sampling); and (iii) the CH₄ concentration of headspace samples taken at the start (t₁) and end (t₂) of flux-chamber operation.

To calculate the CH₄ flux rate, firstly the volume of CH₄ in the flux-chamber at times t₁ and t₂ was estimated as follows:

\[ V_{field} = \left[ C_s \times 10^{-6} \right] \times V_{chamber} \]

where \( V_{field} \) is the volume of CH₄ in the flux-chamber at the time the headspace sample is taken (L), \( C_s \) is the CH₄ concentration of the headspace sample (ppm) and \( V_{chamber} \) is the volume of the flux-chamber volume (L).

The volume of \( V_{field} \) at times t₁ and t₂ was then adjusted using the Ideal Gas Equation:

\[ V_{STP} = V_{field} \times \left( \frac{P_f}{P_{STP}} \right) \times \left( \frac{T_{STP}}{T_f} \right) \]

where \( V_{STP} \) is the volume of CH₄ in the flux-chamber (L) at standard temperature and pressure (STP), \( P_f \) and \( T_f \) are barometric pressure (kPa) and temperature (K) at the time of headspace sampling, respectively, and \( T_{STP} \) and \( P_{STP} \) are 273.15 K and 100 kPa, respectively.

The number of moles of CH₄ in the flux-chamber (Mol_{CH₄}) at t₁ and t₂ were then calculated by dividing the volume of CH₄ in the flux-chamber at STP (\( V_{STP} \)) by the volume of one mole of ideal gas (22.7 L).

Finally, the daily averaged flux of CH₄ per square metre per day was calculated as follows:
\[ T_{CH4} = \left( [Mol_{CH4} at t_2 - Mol_{CH4} at t_1] / \left( [t_2 - t_1] / t_{day} \right) \right) \times M_{CH4} \]  

(Eq. 10),

where \( T_{CH4} \) is the daily rate of \( CH_4 \) flux to the atmosphere (mg \( CH_4 \) m\(^2\) d\(^{-1}\)), \( t_2 - t_1 \) is the time interval between the first and last headspace sample (seconds), \( t_{day} \) is the number of seconds in a day (86400), \( A \) is the surface area enclosed by the collar (m\(^2\)) and \( M_{CH4} \) is the mass of one mole of \( CH_4 \) (mg).

A total of 505 \( CH_4 \) fluxes were calculated from the weekly/biweekly flux-chamber measurements throughout the year. These data were used to test HYPOTHESES 1, 2 and 3 (CHAPTER 4).

3.5.2 CALCULATING FUNNEL-GAS VOLUME AT THE TIME OF MEASUREMENT

As noted in Section 3.3.3, it was necessary to convert field-measurements of funnel-gas (mm) into volumetric units (mL). For all measurements < 100 mm (i.e. where funnel-gas did not extend below the measurement tube) the relationship between actual volume of funnel-gas (mL) and measured funnel-gas (mm) was assumed to be \( y = x \) (i.e. 1 mL = 1 mm). This assumption was tested in the field and laboratory (using different funnel-traps, under different temperatures and pressures) and was accurate to within ± 0.2 mL. For funnel-gas measurements ≥ 100 mm (i.e. when the funnel-gas extended into the base of the funnel), the relationship between the actual volume of funnel-gas and the observed funnel-gas measurement was exponential. The exponential model \( y = 11.385e^{0.0208x} \) was used to adjust each funnel-gas measurement ≥ 100 mm (Figure 14), derived from laboratory tests on one funnel-trap prior to installation at Cors Fochno. The model was re-tested using two different funnel-traps after the study was complete (November 2009). The exponential relationships for each of the funnel-traps were very similar (constants were 11.4 and 11.7 and the \( r^2 > 0.99 \)).
3.5.3 Calculating ebullition fluxes to the water table

For each funnel-trap, the change in the volume of funnel-gas each week was converted into flux per unit area as follows:

\[
B_f = \frac{\Delta V_{f-gas}}{A}
\]  

(Eq. 11),

where \(B_f\) is the bubble flux to the water table in units of mL gas m\(^{-2}\), \(\Delta V_{f-gas}\) is the change in funnel-gas volume between two measurements (mL) and \(A\) is basal area of the funnel-trap (m\(^2\)).

For the pressure events, hourly-averaged rates of bubble flux (mL gas m\(^{-2}\) h\(^{-1}\)) were calculated by first applying Eq. 11 and then dividing by the time elapsed between measurements (hr). A total of 459 weekly bubble fluxes were calculated for the May – September 2009 period and 468 and 364 hourly-averaged rates of bubble flux were calculated for the two pressure events, respectively. The pressure event data and 414 of the weekly bubble fluxes (for the period 28\(^{th}\) May – 12\(^{th}\) September 2009) were used in tests of Hypothesis 6 (Chapter 6).

To calculate a daily averaged rate of CH\(_4\) ebullition (units of mg CH\(_4\) m\(^{-2}\) d\(^{-1}\)) from the change in funnel-gas volume the following were required: (i) the volume of the
funnel-gas at the time of measurement (L); (ii) funnel-gas temperature ($T_f$) and pressure ($P_f$) (estimated from the Cors Fochno barometric pressure and air temperature log); and (iii) the estimated $CH_4$ concentration of the funnel-gas at the time of measurement (based on the $CH_4$ concentration of the monthly samples of funnel-gas).

Firstly, the volume of bubble $CH_4$ collected by the funnel-trap between measurements ($B_{CH4}$) was estimated as follows:

$$B_{CH4} = (C_{f-gas} \times 10^{-6}) \times \Delta V_{f-gas} \quad (Eq. 12),$$

where $B_{CH4}$ is the volume of bubble $CH_4$ (L), $C_{f-gas}$ is the estimated $CH_4$ concentration of the funnel-gas (ppm) and $\Delta V_{f-gas}$ is the change in funnel-gas volume between measurements (L).

The volume of $B_{CH4}$ was then adjusted using the Ideal Gas Equation as follows:

$$V_{STP} = B_{CH4} \times \left(\frac{P_f}{T_f}\right) \times \left(\frac{T_{STP}}{P_{STP}}\right) \quad (Eq. 13),$$

where $V_{STP}$ is the volume of bubble $CH_4$ trapped by the funnel-trap (L) at standard temperature and pressure (STP), $P_f$ and $T_f$ are barometric pressure (kPa) and temperature (K) at the time of measurement, respectively, and $T_{STP}$ and $P_{STP}$ are 273.15 K and 100 kPa, respectively.

The number of moles of bubble $CH_4$ captured by the funnel-trap ($Mol_{CH4}$) was then estimated by dividing the volume of bubble $CH_4$ in the funnel-trap at STP ($V_{STP}$) by the volume of one mole of ideal gas (22.7 L).

Finally, the daily averaged rate of $CH_4$ ebullition was calculated as follows:

$$F_{CH4} = \left(Mol_{CH4} \times M_{CH4}\right) / (t_2 - t_1) / A \quad (Eq. 14),$$

where $F_{CH4}$ is the daily averaged rate of $CH_4$ ebullition into the funnel-trap (mg $CH_4$ m$^{-2}$ d$^{-1}$), $M_{CH4}$ is the mass of one mole of $CH_4$ (mg), A is the basal area of the funnel-trap (m$^2$) and $t_2 - t_1$ is the time interval between the weekly measurements (days).
A total of 459 weekly measurements of CH$_4$ ebullition (expressed as daily rates) were calculated for the May – September 2009 period. 414 of the rates of CH$_4$ ebullition (for the period 28th May – 12th September 2009) were used in the tests of HYPOTHESES 4 and 5 (CHAPTER 5).

3.5.4 SCALING-UP USING HIGH-RESOLUTION AERIAL PHOTOGRAHS

One of the primary reasons for quantifying emissions variability at Cors Fochno was to provide a reliable, scaled-up emissions estimates for the peatland. In the past, scaling-up has been based on the areal extent of different structural features or large-scale changes in vegetation cover/peatland type calculated from detailed maps of land surface cover (e.g. Bubier et al., 1997; Roulet et al., 1994). Scaling-up in this way can produce large uncertainties in emissions estimates (Becker et al., 2008) - particularly if some peatland features are ‘hotspots’ of CH$_4$ emissions (e.g. McNamara et al., 2008).

For this thesis, scaling-up was based on data from high resolution aerial photographs taken across 100 m × 70 m and 30 m × 30 m areas of the bog dome by Ruth Boogert (University of London) in August 2009. Photographs were taken using a Sutton Flowform 30 frameless parafoil kite fitted with a Canon EOS Rebel XT SLR camera with an 8.0 Megapixel sensor and a wide angle lens (Tamron SP AF 10-24 mm, F3.5-4.5 Di II LD Aspherical (IF)). Photographs were taken at two altitudes – 50 m and 200 m – to produce low- and high-resolution images of the study area. The on-the-ground resolution of the orthophotographs was 5 cm × 5 cm (pixel size) for the lower altitude (50 m) (Figure 15) and 12 cm × 12 cm at the higher altitude (200 m).

Low altitude photographs showed the location of each collar and colour differences between the main vegetation classes across the bog dome. In photographs taken from a vertical shooting angle, mud-bottomed hollows appeared as very dark brown areas, Sphagnum lawns were orange/golden, lawns dominated by Rhynchospora alba were light green, drier lawns dominated by Eriophorum spp were grey, and dark-green areas were hummocks dominated by Calluna vulgaris and Myrica gale. The distinct colours allowed the different microform-types investigated in this thesis to be differentiated reasonably well by Boogert (2009) using a supervised classification method. However, there was uncertainty in the
classification of mud-bottomed hollows due to shadowing in the images caused by large C. vulgaris plants on some hummocks (shadows also appeared as very dark brown areas on the images).

Photo credit: Boogert (2009).

Figure 15: Section of a composite orthophotograph taken during low altitude kite flights across Cors Fochno.
Chapter 4  METHANE FLUXES FROM MICROFORMS OF A PATTERNED RAISED BOG

As described in Section 3.2.3, between 31^st^ March 2008 and 20^th^ March 2009 flux-chamber measurements were taken from 20 collars equally distributed across four microform- types – sedge lawn, mud-bottomed hollow, Sphagnum lawn, and hummock. This chapter reports on the spatial and temporal variation of CH₄ emissions from the different microform- types and the controls on this variability. Specifically, three main hypotheses were tested:

- **HYPOTHESIS 1:** At an annual scale, CH₄ emissions vary significantly between microform- types.

- **HYPOTHESIS 2:** Differences in plant cover, peat temperature and water table position explain the spatial variability in CH₄ emissions between microforms- types.

- **HYPOTHESIS 3:** Air temperature, solar radiation, rainfall, wind speed, wind direction and barometric pressure are significant controls on temporal variability of daily CH₄ fluxes from each microform- type.

The chapter also presents scaled- up estimates of CH₄ emissions for the bog dome to assess the contribution of different microforms to total emissions. Full details of experimental and analytical methods pertaining to the results in this chapter are described in Chapter 3, sections 3.2, 3.4 and 3.5. Briefly, chamber- fluxes were measured during 29 weeks of the year: eight weeks in spring (March, April, May), seven in summer (June, July, August), eight in autumn (September, October, November), and six in winter (December, January, February). Chamber- fluxes were measured over 25 – 40 min (expressed as a daily rate, mg m⁻² d⁻¹). In this chapter, **HYPOTHESIS 1** was tested by applying two one-way ANOVAs to the cumulative (time- integrated) CH₄ emissions totals (annual CH₄ emissions, g m⁻²) and average CH₄ fluxes (mean CH₄ flux, mg m⁻² d⁻¹) respectively for each collar (n = 20). **HYPOTHESIS 2** was tested using stepwise multiple regression analysis on the annual CH₄ emissions data and sixteen variables describing microform- type, plant cover, mean water table position and mean peat temperature for each collar. **HYPOTHESIS**
3 was tested using an additional stepwise multiple regression analysis on the full CH4 flux dataset (n = 505) and sixteen abiotic variables.

4.1 RESULTS

The average CH4 flux during the year was 31.7 ± 1.8 (SE) mg m\(^{-2}\) d\(^{-1}\) (n = 505), with CH4 fluxes ranging from -8.9 to 190.1 mg m\(^{-2}\) d\(^{-1}\). The 25\(^{th}\) percentile flux was 7.5 mg m\(^{-2}\) d\(^{-1}\), median flux 16.9 mg m\(^{-2}\) d\(^{-1}\), and 75\(^{th}\) percentile 37.2 mg m\(^{-2}\) d\(^{-1}\).

Cumulative (time-integrated) annual CH4 emissions values for the twenty collars ranged from 5.1 – 215.2 g m\(^{-2}\) (n = 20). The mean annual CH4 emissions value was 10.8 (± 1.3) g m\(^{-2}\), 25\(^{th}\) percentile 6.5 g m\(^{-2}\), median 10.7 g m\(^{-2}\) and 75\(^{th}\) percentile 14.9 g m\(^{-2}\).

4.1.1 SEASONAL CH4 FLUXES

On average, CH4 fluxes were lowest in winter and highest in summer (see Table 4). Nearly half of the CH4 emitted during the year was during summer (48.1% of annual CH4 emissions from all twenty collars combined). Between summer and autumn, the average flux decreased by more than 50%. Interestingly, the average flux during winter was only marginally lower than during spring.

<table>
<thead>
<tr>
<th>Season</th>
<th>Mean</th>
<th>SE of mean</th>
<th>n</th>
<th>Median</th>
<th>Min.</th>
<th>Max.</th>
<th>25th percentile</th>
<th>75th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>17.9</td>
<td>1.7</td>
<td>135</td>
<td>12.4</td>
<td>-3.9</td>
<td>133.1</td>
<td>5.6</td>
<td>22.0</td>
</tr>
<tr>
<td>Summer</td>
<td>67.1</td>
<td>5.4</td>
<td>120</td>
<td>47.6</td>
<td>-4.2</td>
<td>190.1</td>
<td>16.7</td>
<td>117.1</td>
</tr>
<tr>
<td>Autumn</td>
<td>30.6</td>
<td>2.5</td>
<td>136</td>
<td>21.7</td>
<td>-8.9</td>
<td>139.4</td>
<td>10.6</td>
<td>38.7</td>
</tr>
<tr>
<td>Winter</td>
<td>12.0</td>
<td>1.1</td>
<td>114</td>
<td>9.8</td>
<td>0.3</td>
<td>90.3</td>
<td>5.3</td>
<td>15.8</td>
</tr>
</tbody>
</table>

Fluxes from hummocks were very similar between spring and winter (seasonal mean fluxes 6.0 ± 1.6 (n = 34) and 8.3 ± 1.6 mg m\(^{-2}\) d\(^{-1}\), respectively), but notably different from mud-bottomed hollows (spring and winter mean fluxes 26.4 ± 4.0 (n = 28) and 13.5 ± 3.5 mg m\(^{-2}\) d\(^{-1}\), respectively) and Sphagnum lawns (spring and winter mean fluxes 17.5 ± 4.0 (n = 39) and 9.4 ± 0.9 mg m\(^{-2}\) d\(^{-1}\), respectively). Spring and winter fluxes from sedge lawns were more similar (means 23.5 ± 1.9 (n = 34) and 16.4 ± 1.5 mg m\(^{-2}\) d\(^{-1}\), respectively). Given the large standard errors on each of the seasonal means, it was useful to test
for a statistical difference between the seasons. Repeated-measures ANOVA on seasonally-averaged CH$_4$ fluxes (one value per collar per season) showed that differences were significant ($p < 0.01$, post hoc Bonferroni to constrain Type I error) between all seasons except winter and spring (Figure 16). As a proportion of total annual CH$_4$ emissions from all twenty collars (g m$^{-2}$), winter emissions represented 9.4% of the annual CH$_4$ budget compared with 17.9% during spring. Winter emissions from sedge lawns were 10.3% of the annual total for the microform-type compared with 8.2% for mud-bottomed hollows, 8.6% for Sphagnum lawns and 11.4% for hummocks.

![Box plot of seasonally averaged CH$_4$ fluxes for each collar.](image)

Figure 16: Box plot of seasonally averaged CH$_4$ fluxes for each collar.

Boxes represent the interquartile range (IQR) and the thick horizontal lines indicate the group median. Bottom whiskers represent values in the lower quartile, while top whiskers represent those in the upper quartile which are not greater than $1.5 \times$ IQR. Values $>1.5 \times$ IQR are outliers (shown by a circle) and values $>3 \times$ IQR are extreme cases (shown by an asterisk).

4.1.2 Spatial Variability of CH$_4$ Fluxes During Measurement Weeks

During most measurement weeks, spatial variation in CH$_4$ flux between collars of the same microform-type (within-group variability) was high, particularly in summer (Figure 17). Generally in spring, within-group variability was high for mud-bottomed hollows and Sphagnum lawns and relatively low for hummocks and sedge lawns. All microform-types exhibited high within-group variability in
Figure 17: Time series of within-group variability in each measurement week. Bars represent the range of CH$_4$ fluxes in each of 29 measurement weeks.
mid and late summer, which subsequently declined during autumn. Atypically high fluxes from hummocks were from collars with a high abundance of Rhynchospora alba (80 – 90% cover) – a CH₄-transporting sedge species. Within-group variability was typically low in winter for all microform types, except at the end of the season for mud-bottomed hollows.

4.1.3 Frequency distributions of CH₄ fluxes from each microform type

All microform types exhibited a similar range of individual CH₄ fluxes over the course of the year (Table 5). Hummocks exhibited the largest coefficient of variation – a measure of temporal and spatial variation in CH₄ flux - and the lowest median CH₄ flux. Sedge lawns exhibited the lowest coefficient of variation and highest median CH₄ flux. Frequency distributions were all strongly positively skewed (Figure 18). Fluxes were more variable from mud-bottomed hollows than from sedge lawns, but the frequency distributions were relatively similar. High individual fluxes are probably the result of either plant-mediated transport of CH₄ or ebullition. However, given that only one collar was entirely unvegetated (Collar 11, see Table 6 Section 4.1.4), it is not possible to estimate the relative importance of each transport pathway.

Table 5: Summary of CH₄ fluxes from each microform type.

<table>
<thead>
<tr>
<th>Microform type</th>
<th>Median (mg m⁻² d⁻¹)</th>
<th>Min.</th>
<th>Max.</th>
<th>25th percentile</th>
<th>75th percentile</th>
<th>CV(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedge lawn</td>
<td>26.7</td>
<td>2.8</td>
<td>181.6</td>
<td>16.1</td>
<td>45.8</td>
<td>97</td>
</tr>
<tr>
<td>Mud-bottomed hollow</td>
<td>22.2</td>
<td>-2.4</td>
<td>187.9</td>
<td>9.5</td>
<td>57.3</td>
<td>109</td>
</tr>
<tr>
<td>Sphagnum lawn</td>
<td>14.6</td>
<td>-8.9</td>
<td>168.1</td>
<td>7.8</td>
<td>32.0</td>
<td>124</td>
</tr>
<tr>
<td>Hummock</td>
<td>6.0</td>
<td>-4.2</td>
<td>190.1</td>
<td>1.5</td>
<td>16.6</td>
<td>206</td>
</tr>
</tbody>
</table>
4.1.4 COMPARING PLANT COVER, WATER TABLE AND PEAT TEMPERATURE BETWEEN MICROFORM-TYPES

Plant survey data from November 2008 were used to determine plant species abundance within each collar (see Chapter 3 Section 3.2.6). Sedges are widely referenced as the most important peatland species with respect to $\text{CH}_4$ dynamics and were thought likely to influence variability in $\text{CH}_4$ fluxes. *Rhynchospora alba* was the most abundant sedge and grew within the perimeter of all but one of the collars. *Eriophorum angustifolium* and *Eriophorum vaginatum* were less common but were found in collars of all microform-types - most frequently within sedge lawns and mud-bottomed hollows (Table 6). Average peat temperature (APT) was estimated from near-surface temperatures (20 cm depth) recorded during each measurement week from 6th August 2008 (11 – 13 measurements per collar). Average distance to the water table from the peat surface (ADWT) was estimated from dip-well measurements taken from 29th April 2008 (23–26 measurement...
Table 6: Variables used in stepwise regression models of mean daily CH\textsubscript{4} flux and annual CH\textsubscript{4} emission.

<table>
<thead>
<tr>
<th>Collar</th>
<th>Microform type</th>
<th>Average peat temp (°C)</th>
<th>Average depth to water-table (cm)</th>
<th>Eriophorum spp*</th>
<th>Rhynchospora alba</th>
<th>Calluna vulgaris</th>
<th>Erica tetralix</th>
<th>Myrica gale</th>
<th>Narthecium ossifragum</th>
<th>Menyanthes trifoliata</th>
<th>Andromeda polifolia</th>
<th>Vaccinium oxyccos</th>
<th>Drosera anglica</th>
<th>Cladonia rangiferina</th>
<th>Mud/algae</th>
<th>Sphagnum moss</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Sedge lawn</td>
<td>10.7</td>
<td>4.4</td>
<td>47</td>
<td>100</td>
<td>0</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
<td>Sedge lawn</td>
<td>11.3</td>
<td>2.2</td>
<td>8</td>
<td>100</td>
<td>0</td>
<td>46</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>16</td>
<td>Sedge lawn</td>
<td>11.3</td>
<td>3.0</td>
<td>22</td>
<td>90</td>
<td>8</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>55</td>
<td>81</td>
</tr>
<tr>
<td>17</td>
<td>Sedge lawn</td>
<td>9.2</td>
<td>9.4</td>
<td>18</td>
<td>99</td>
<td>17</td>
<td>69</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>Sedge lawn</td>
<td>10.0</td>
<td>7.3</td>
<td>38</td>
<td>100</td>
<td>0</td>
<td>41</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Group mean</td>
<td>10.5</td>
<td>5.2</td>
<td>26</td>
<td>98</td>
<td>5</td>
<td>42</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.4</td>
<td>1.4</td>
<td>7</td>
<td>2</td>
<td>3</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>M-b hollow</td>
<td>11.2</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>27</td>
</tr>
<tr>
<td>12</td>
<td>M-b hollow</td>
<td>11.2</td>
<td>0.6</td>
<td>49</td>
<td>61</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>13</td>
<td>M-b hollow</td>
<td>11.0</td>
<td>0.5</td>
<td>30</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>46</td>
</tr>
<tr>
<td>19</td>
<td>M-b hollow</td>
<td>10.4</td>
<td>0.0</td>
<td>4</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>20</td>
<td>M-b hollow</td>
<td>10.4</td>
<td>0.3</td>
<td>58</td>
<td>45</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Group mean</td>
<td>10.8</td>
<td>0.4</td>
<td>28</td>
<td>47</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.2</td>
<td>0.1</td>
<td>12</td>
<td>17</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Sphagnum lawn</td>
<td>10.5</td>
<td>5.1</td>
<td>41</td>
<td>85</td>
<td>0</td>
<td>5</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sphagnum lawn</td>
<td>10.6</td>
<td>5.3</td>
<td>28</td>
<td>89</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Sphagnum lawn</td>
<td>11.5</td>
<td>9.6</td>
<td>0</td>
<td>98</td>
<td>0</td>
<td>50</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Sphagnum lawn</td>
<td>9.9</td>
<td>2.8</td>
<td>59</td>
<td>83</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Sphagnum lawn</td>
<td>9.7</td>
<td>3.8</td>
<td>46</td>
<td>91</td>
<td>0</td>
<td>17</td>
<td>0</td>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Group mean</td>
<td>10.5</td>
<td>5.3</td>
<td>35</td>
<td>89</td>
<td>0</td>
<td>16</td>
<td>2</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.3</td>
<td>1.2</td>
<td>10</td>
<td>3</td>
<td>0</td>
<td>9</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hummock</td>
<td>10.7</td>
<td>15.5</td>
<td>12</td>
<td>36</td>
<td>59</td>
<td>69</td>
<td>1</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Hummock</td>
<td>11.1</td>
<td>11.0</td>
<td>0</td>
<td>83</td>
<td>83</td>
<td>10</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Hummock</td>
<td>9.8</td>
<td>25.8</td>
<td>0</td>
<td>37</td>
<td>78</td>
<td>30</td>
<td>0</td>
<td>27</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Hummock</td>
<td>10.5</td>
<td>17.7</td>
<td>31</td>
<td>80</td>
<td>0</td>
<td>75</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Hummock</td>
<td>11.1</td>
<td>10.8</td>
<td>14</td>
<td>99</td>
<td>22</td>
<td>61</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Group mean</td>
<td>10.7</td>
<td>16.2</td>
<td>12</td>
<td>67</td>
<td>48</td>
<td>49</td>
<td>2</td>
<td>8</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.2</td>
<td>2.7</td>
<td>6</td>
<td>13</td>
<td>16</td>
<td>12</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

* Areal cover of Eriophorum vaginatum and Eriophorum angustifolium are combined due to difficulties in distinguishing the two species.
per collar). APT values were similar across the 20 collars. In contrast, ADWT was highly variable. As expected, mean ADWT was highest for hummocks and lowest for mud-bottomed hollows and similar for the sedge and Sphagnum lawn collars.

Differences and similarities in temperature, water table depth and plant species abundance between the microform-types were tested using a series of one-way ANOVA and correlations. In the ANOVA, Bonferroni and Games-Howell post hoc adjustments were applied to correct for Type I errors. It was found that the percentage cover of the heath Erica tetralix was significantly different between mud-bottomed hollows and sedge lawns (p < 0.05). ADWT was significantly different between hummocks and all other microform-types (p < 0.05). Percentage cover of Sphagnum spp. and mud/algae were strongly positively correlated (r > 0.99, p < 0.001). There was significantly more mud/algae and less Sphagnum moss in mud-bottomed hollows compared with the other microform-types (p < 0.01).

4.1.5 **Hypothesis 1: At an annual scale, CH₄ emissions vary significantly between microform-types.**

Cumulative (time-integrated) annual CH₄ emissions (g m⁻²) (52 weeks) and mean CH₄ flux (mg m⁻² d⁻¹) values were calculated for each collar (5 collars per microform-type). Average annual CH₄ emissions were 13.3 ± 1.6 g m⁻² (n = 5) for sedge lawns, 14.0 ± 3.0 (SE) g m⁻² (n = 5) for mud-bottomed hollows, 9.9 ± 2.2 g m⁻² (n = 5) for Sphagnum lawns, and 5.9 ± 2.1 g m⁻² (n = 5) for hummocks. Average mean CH₄ flux was 42.1 ± 4.8 mg m⁻² d⁻¹ (n = 5) for sedge lawns, 41.8 ± 8.1 mg m⁻² d⁻¹ (n = 5) for mud-bottomed hollows, 26.0 ± 5.7 mg m⁻² d⁻¹ (n = 5) for Sphagnum lawns, and 18.1 ± 7.0 mg m⁻² d⁻¹ (n = 5) for hummocks (Figure 19a & 19b).

To test for a statistical difference between the microform-types, two one-way ANOVA tests were run on the annual CH₄ emissions and mean daily CH₄ flux data. A marginally significant (p = 0.05) main effect of microform-type was revealed in each test. After post hoc procedures (Bonferroni and Tukey’s HSD) to constrain Type I error, differences between the microform-types were not significant (p > 0.05) and the hypothesis was thus rejected.
4.1.6 EXTRAPOLATED CH₄ EMISSIONS ESTIMATE FOR BOG DOME

Boxes represent the interquartile range (IQR), i.e. the second and fourth largest values for each microform-type. Thick horizontal lines indicate the group median. Whiskers represent the highest and lowest values in the group. For mud-bottomed hollows in 13b, the highest and lowest mean CH₄ flux values (corresponding to collars 11 and 13) were extreme cases (> 3 × IQR and < 3 × IQR, respectively) and are shown with asterisks.
From kite-based aerial photography of a 12,895 m² area of the bog dome (Chapter 3, Section 3.5.4), Boogert (2009) estimated percentage cover of sedge lawns, mud-bottomed hollows, Sphagnum lawns and hummocks to be 72.4% 3.4% 4.0% and 18.7% respectively. The remaining 1.5% of the peatland surface was classified as permanent boardwalk (from which CH₄ emissions are assumed to be zero). Given that the difference between the microform-types was insignificant, a scaled-up estimate of CH₄ emissions from the bog dome could be reasonably estimated from either (i) the surface area and average annual CH₄ emissions values for each microform-type (i.e. microform-weighted estimate) or (ii) the full dome area and average annual CH₄ emissions value for all twenty collars (a non-weighted estimate). In the microform-weighted estimate, after factoring in standard errors it was estimated that between 127.2 and 172.1 kg CH₄ y⁻¹ was emitted from the 12,895 m³ bog dome. In the non-weighted estimate, the range was 120.7 – 153.7 kg CH₄ y⁻¹ (Table 7).

Experiencing the individual components of the microform-weighted calculation, the extrapolated CH₄ emissions from sedge lawns accounted for c. 81-91% of total CH₄ emissions for the bog dome (depending on how total CH₄ emissions was calculated). Due to their relatively small spatial area, CH₄ emissions from the remaining microform-types were relatively unimportant.
4.1.7 Hypothesis 2: Differences in plant cover, water table position and near-surface peat temperature explain the spatial variability of CH$_4$ emissions between microform-types.

Stepwise multiple regression (SWR) analysis was performed on the mean CH$_4$ flux (SW2a) and annual CH$_4$ emissions data (SWR2b) using the biotic and abiotic variables shown in Table 6 and an additional ‘microform-type’ variable (sixteen predictive variables in total). The model acceptance criterion for the predictor variables was $p \leq 0.05$. Significant predictors for the two regressions (SWR2a and SWR2b) are shown in Table 8 and Table 9, respectively.

### Table 8: Stepwise multiple regression model of mean CH$_4$ fluxes (SWR2a).

<table>
<thead>
<tr>
<th>Predictor(s)</th>
<th>$r^2$</th>
<th>$p$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 ADWT</td>
<td>0.33</td>
<td>0.008</td>
<td>14.34</td>
</tr>
<tr>
<td>Step 2 ADWT and %Rhynchospora</td>
<td>0.51</td>
<td>0.002</td>
<td>12.67</td>
</tr>
<tr>
<td>Step 3 ADWT, %Rhynchospora and %Sphagnum</td>
<td>0.68</td>
<td>&lt;0.001</td>
<td>10.61</td>
</tr>
<tr>
<td>Step 4 %Rhynchospora and %Sphagnum</td>
<td>0.67</td>
<td>&lt;0.001</td>
<td>10.38</td>
</tr>
<tr>
<td>Step 5 %Rhynchospora, %Sphagnum and %Andromeda</td>
<td>0.75*</td>
<td>&lt;0.001</td>
<td>9.37</td>
</tr>
</tbody>
</table>

* denotes the $r^2$ of the ‘best fit’ model of mean daily CH$_4$ fluxes for the twenty collars.

### Table 9: Stepwise multiple regression model of annual CH$_4$ emissions (SWR2b).

<table>
<thead>
<tr>
<th>Predictor(s)</th>
<th>$r^2$</th>
<th>$p$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 ADWT</td>
<td>0.32</td>
<td>0.009</td>
<td>4.84</td>
</tr>
<tr>
<td>Step 2 ADWT and %Rhynchospora</td>
<td>0.51</td>
<td>0.002</td>
<td>4.24</td>
</tr>
<tr>
<td>Step 3 ADWT, %Rhynchospora and %Sphagnum</td>
<td>0.68</td>
<td>&lt;0.001</td>
<td>3.53</td>
</tr>
<tr>
<td>Step 4 %Rhynchospora and %Sphagnum</td>
<td>0.68*</td>
<td>&lt;0.001</td>
<td>3.45</td>
</tr>
</tbody>
</table>

* denotes the $r^2$ of the ‘best fit’ model of annual CH$_4$ emissions values for the twenty collars.

The best individual predictor of mean CH$_4$ flux and annual CH$_4$ emissions was average depth to water table (ADWT), but the best fit multivariate models contained only biotic factors. ADWT had a moderately strong inverse correlation with annual CH$_4$ emissions ($r_s = -0.54$, $p < 0.05$, 1-tailed, $n = 20$), but the relationship between the variables was much weaker when two lowest emitting hummocks (collars 4 and 7) were excluded ($r_s = -0.37$, $p =0.06$). Sphagnum moss and ADWT variables were strongly correlated ($r_s = 0.77$, $p < 0.001$) and covariance was high in Step 3 of each model (the average variance inflation factors (VIF) were 2.66 and 2.28, respectively). The Sphagnum moss...
variable produced the better model of the data when combined with Rhynchospora alba. In SWR2a, inclusion of percent cover of Andromeda polifolia (Bog Rosemary) in Step 5 significantly improved a variate model containing Rhynchospora alba and Sphagnum moss. However, it was not a significant contributor to the best fit model of annual CH$_4$ emissions (SWR2b). There is no known study that has linked Andromeda polifolia to CH$_4$ flux dynamics and the exact processes which the plant species may have interacted with are unclear. Average peat temperature (APT) was not a significant explanatory variable in either model, presumably due to small variation in APT between individual collars.

To test if the biotic and abiotic variables could also explain variation between collars of the same microform-type (i.e. within-group variability), the multiple regression analyses were re-run after separating the data by microform-type. The microform-type classification variable was excluded from the analysis as were any invariant factors within the partial models (e.g. percent cover of mud/algae for the mud-bottomed hollow model). For the hummock partial models, percent cover of Rhynchospora alba accounted for 87% and 92% of the variation in mean daily CH$_4$ flux and annual CH$_4$ emissions, respectively ($p < 0.05$) (Figure 20).

Figure 20: Relationships between percent cover of Rhynchospora alba and annual CH$_4$ emissions and mean CH$_4$ flux from hummocks and mud-bottomed hollows.

Diamonds represent annual CH$_4$ emissions values for each collar while circles represent mean CH$_4$ fluxes.
In the mud-bottomed hollow partial models, Rhynchospora alba explained 93% and 88% of the variation, respectively (p < 0.05). The partial models suggest that differences in the abundance of R. alba controlled within-group variation in CH₄ emissions. None of the plant cover variables were significant predictors of within-group variability for Sphagnum lawns and sedge lawns (p > 0.05).

4.1.8 **Hypothesis 3: Air temperature, solar radiation, rainfall, wind speed, wind direction and barometric pressure are significant controls on temporal variability of daily CH₄ fluxes from each microform-type.**

Stepwise multiple regression analysis was performed on the CH₄ flux data (n = 505) and 15 abiotic variables that described air temperature, solar radiation, rainfall, barometric pressure and wind speed and direction during the course of the year (Table 10). The main regression on the full CH₄ flux dataset (SWR3a) revealed that

<table>
<thead>
<tr>
<th>Abiotic factor</th>
<th>Predictor variable</th>
<th>Units</th>
<th>Abbrev</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Barometric pressure</strong></td>
<td>Barometric pressure at time of chamber-flux measurement</td>
<td>hPa</td>
<td>Pt</td>
</tr>
<tr>
<td></td>
<td>Average barometric pressure over previous 3 daysᵃ</td>
<td></td>
<td>APT₃</td>
</tr>
<tr>
<td></td>
<td>Average barometric pressure over previous weekᵇ</td>
<td></td>
<td>APT₇</td>
</tr>
<tr>
<td><strong>Air temperature</strong></td>
<td>Averaged air temperature for date of chamber-flux measurement</td>
<td>°C</td>
<td>ATₜ</td>
</tr>
<tr>
<td></td>
<td>Average air temperature for previous 3 days</td>
<td>°C</td>
<td>ATₜ⁻³</td>
</tr>
<tr>
<td></td>
<td>Average air temperature for previous week</td>
<td>°C</td>
<td>ATₜ⁻⁷</td>
</tr>
<tr>
<td><strong>Rainfall</strong></td>
<td>Total rainfall on day before chamber-flux measurementᵈ</td>
<td>mm</td>
<td>RT₁</td>
</tr>
<tr>
<td></td>
<td>Total rainfall during previous 3 daysᵈ</td>
<td>mm</td>
<td>RT₃</td>
</tr>
<tr>
<td></td>
<td>Total rainfall during previous weekᵈ</td>
<td>mm</td>
<td>RT₇</td>
</tr>
<tr>
<td><strong>Solar radiation</strong></td>
<td>Solar radiation at time of chamber-flux measurement</td>
<td>W m⁻²</td>
<td>ST₁</td>
</tr>
<tr>
<td></td>
<td>Total solar radiation on previous dayᶜ</td>
<td>W m⁻²</td>
<td>ST₃</td>
</tr>
<tr>
<td></td>
<td>Total solar radiation during previous 3 daysᵃ</td>
<td>W m⁻²</td>
<td>ST₃</td>
</tr>
<tr>
<td></td>
<td>Total solar radiation during previous weekᵇ</td>
<td>W m⁻²</td>
<td>ST₇</td>
</tr>
<tr>
<td><strong>Wind</strong></td>
<td>Wind speed at time of chamber-flux measurement</td>
<td>mph</td>
<td>WS</td>
</tr>
<tr>
<td></td>
<td>Wind direction at time of chamber-flux measurement</td>
<td>Cardinal</td>
<td>WD</td>
</tr>
</tbody>
</table>

ᵃ Based on 72 hr period prior to start time of chamber-flux measurement
ᵇ Based on 168 hr period prior to start time of chamber-flux measurement
ᶜ Based on 24 hr period prior to start time of chamber-flux measurement
ᵈ Includes rainfall up to 10:00 GMT on the date of chamber-flux measurement. Rainfall data are from the Cors Fochno and Talybont rain gauges.
weekly-averaged air temperature (AT\textsubscript{t-7}) was the best individual predictor of variation in daily CH\textsubscript{4} fluxes, predicting 23% of the variance (Table 11). Stepwise inclusion of weekly rainfall total (R\textsubscript{t-7}), weekly-averaged barometric pressure (AP\textsubscript{t-7}), total solar radiation on the day prior to chamber-flux measurement (St\textsubscript{-1}) and total rainfall on the day prior to chamber-flux measurement (R\textsubscript{t-1}) each made significant improvements to the regression model (p < 0.05). But, the best fit multivariate model explained only 29% of variability in the CH\textsubscript{4} flux data.

Over the year, there was a moderately strong correlation between weekly-totalled solar radiation and weekly-averaged air temperatures (Pearson’s r = 0.53, p < 0.001). In summer the correlation between the variables was not significant (Pearson’s r = 0.09, p > 0.05). The two rainfall variables (R\textsubscript{t-7} and R\textsubscript{t-1}) were positively correlated (Spearman’s rank, r\textsubscript{s} = 0.63, p < 0.001), but covariance did not adversely affect the model’s reliability. Neither of the wind variables were significant predictors of variation (p > 0.05). The most important abiotic variables driving temporal variations of CH\textsubscript{4} flux are shown at in Figure 21 (Section 4.1.9).

<table>
<thead>
<tr>
<th>Predictor(s)</th>
<th>r\textsuperscript{2}</th>
<th>p</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>AT\textsubscript{t-7}</td>
<td>0.23</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Step 2</td>
<td>AT\textsubscript{t-7} and R\textsubscript{t-7}</td>
<td>0.25</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Step 3</td>
<td>AT\textsubscript{t-7}, R\textsubscript{t-7} and AP\textsubscript{t-7}</td>
<td>0.26</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Step 4</td>
<td>AT\textsubscript{t-7}, R\textsubscript{t-7}, AP\textsubscript{t-7} and St\textsubscript{-1}</td>
<td>0.28</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Step 5</td>
<td>AT\textsubscript{t-7}, R\textsubscript{t-7}, AP\textsubscript{t-7}, St\textsubscript{-1} and R\textsubscript{t-1}</td>
<td>0.29*</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

* denotes the r\textsuperscript{2} of the ‘best fit’ model of CH\textsubscript{4} fluxes measured during the year.

To test the hypothesis for each microform-type, the regression was re-run after separating the full dataset by microform-type. Weekly-averaged air temperature (AT\textsubscript{t-7}) was the most important variable describing variability in the sedge lawn, Sphagnum lawn and hummock partial models, while air temperature averaged over 3 days (AT\textsubscript{t-3}) was the most important variable for the mud-bottomed hollow model (see Table 12). Weekly-averaged barometric pressure (AP\textsubscript{t-7}) was significant to all best fit partial models except for hummocks. Solar radiation variable (St\textsubscript{3} and St\textsubscript{1}) were significant factors in only the sedge and Sphagnum lawn partial models, possibly due to the high cover of sedge species across these microforms. Interestingly, rainfall (R\textsubscript{t-7}) was only significant in the hummock partial model and, although not significant in the main regression (SWR3a) wind direction (WD) was
significant in the sedge lawn partial model. Best-fit models explained half the variation in daily CH$_4$ fluxes from sedge lawns (partial model $r^2 = 0.51$) and approximately a third of the variation from Sphagnum lawns and mud-bottomed hollows (partial model $r^2$ values were 0.36 and 0.34, respectively). The best-fit partial model for the hummock dataset had an $r^2$ of only 0.12 ($p < 0.001$).

Table 12: Best fit multivariate partial models of CH$_4$ fluxes from each microform-type (SWR3b-e).

<table>
<thead>
<tr>
<th>Partial models SWR3b-e</th>
<th>Dependent variable: CH$_4$ flux (mg m$^{-2}$ d$^{-1}$)</th>
<th>Predictors</th>
<th>$r^2*$</th>
<th>p</th>
<th>SE</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedge lawn</td>
<td>AT$<em>{t-7}$, St$</em>{-3}$, AP$_{t-7}$ and WD</td>
<td>0.51</td>
<td>&lt;0.001</td>
<td>29.08</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>Mud-bottomed hollows</td>
<td>AT$<em>{t-3}$ and AP$</em>{t-7}$</td>
<td>0.34</td>
<td>&lt;0.001</td>
<td>37.16</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>Sphagnum lawn</td>
<td>AT$<em>{t-7}$, St and AP$</em>{t-7}$</td>
<td>0.36</td>
<td>&lt;0.001</td>
<td>26.16</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>Hummock</td>
<td>AT$<em>{t-7}$ and Rt$</em>{-7}$</td>
<td>0.12</td>
<td>&lt;0.001</td>
<td>35.18</td>
<td>126</td>
<td></td>
</tr>
</tbody>
</table>

* $r^2$ for the 'best fit' partial model of CH$_4$ fluxes measured during the year

4.1.9 SUMMARY OF HYPOTHESIS TESTS

With respect to HYPOTHESIS 1 there were no significant differences between microform-types and the hypothesis was rejected. Given the outcome of HYPOTHESIS 1, HYPOTHESIS 2 was rejected with respect to microform-types. However, water table position and the abundance of Rhynchospora alba, Sphagnum moss and Andromeda polifolia (in combination) were significant predictors of spatial variations of annually-averaged CH$_4$ flux (mean CH$_4$ flux) between individual microforms. On the basis of the four partial models for the different microform-types, HYPOTHESIS 3 was not accepted in full for any microform-type. For sedge lawns the hypothesis was accepted for all abiotic factors except wind speed and for Sphagnum lawns for all except wind speed and direction. For mud-bottomed hollows, Hypothesis 3 was accepted for air temperature and barometric pressure only and for hummocks for air temperature and rainfall only.
Figure 21: Time-series of the most important abiotic variables driving temporal variations of CH$_4$ flux (SWR3a).
4.2 DISCUSSION

4.2.1 COMPARING EMISSIONS FROM CORS FOCHNO WITH OTHER PATTERNED PEATLANDS

Few studies have investigated small-scale spatial variability in CH$_4$ emissions from temperate patterned peatlands. Notable exceptions include Laine et al. (2007) for an Irish lowland blanket bog (Glencar) and Dinsmore et al. (2009) for a Scottish lowland peatland (Auchencorth Moss). Laine et al. (2007) measured CH$_4$ fluxes on a biweekly-monthly basis between August 2003 and September 2005 from lawn and hummock microforms (18 microforms in the first year of the study, nine in the second). Dinsmore et al. (2009) measured fluxes on a monthly basis between April 2006 and October 2007 from 21 sites across Sphagnum lawn/hollows, two types of hummock similar to those of Cors Fochno (Calluna vulgaris-, sedge-dominated) and riparian sites dominated by the rush Juncus effusus (riparian sites were not comparable to any of the microforms investigated at Cors Fochno). Emissions from Auchencorth Moss were very low compared with those established from the present study on Cors Fochno. Averaged CH$_4$ flux rates (over the full 19-month study period) from hummocks and lawns/hollows at Auchencorth Moss were two orders of magnitude lower than the average rates for comparable microform-types at Cors Fochno (for the Calluna- and sedge-dominated hummocks at Auchencorth Moss average CH$_4$ fluxes were 0.008 and 0.06 mg CH$_4$ m$^{-2}$ d$^{-1}$, respectively, and for lawn/hollows 0.49 mg CH$_4$ m$^{-2}$ d$^{-1}$). Dinsmore et al. (2009) attributed the low emissions from Auchencorth Moss to a generally shallow peat layer. Comparatively low emissions could also be attributed to differences in hydrological and biochemical conditions between Auchencorth Moss and Cors Fochno, particularly the generally low water table position at Auchencorth Moss during growing seasons (Dinsmore et al., 2009).

Average CH$_4$ fluxes from Cors Fochno were closer to those reported by Laine et al. (2007) for three comparable microform-types (hummocks, “low” lawns dominated by R. alba and hollows) on the Glencar bog. Annually-averaged flux rates ranged from 11.6 – 50.4 mg m$^{-2}$ d$^{-1}$ ($n = 3$) at Glencar compared with 18.1 – 41.5 mg m$^{-2}$ d$^{-1}$ for Cors Fochno ($n = 4$). Unlike at Cors Fochno, emissions from Glencar hummocks and hollows were significantly different ($p < 0.05$ after post hoc Tukey) and hollows were the highest emitting microform-type (attributed to the presence of Menyanthes trifoliata in two of the three collars) (Laine et al., 2007). Within-group variability of emissions (between microforms of the same type) at Cors
Fochno was higher than that reported by Laine et al. (2007), particularly for hummocks. Standardized errors on the annual CH$_4$ emissions estimates for hummock, lawn and hollow microform-types ranged from 0.1 – 1.4 g m$^{-2}$ for Glencar compared with 1.6 – 3.0 g m$^{-2}$ for Cors Fochno (hummocks the smallest value in each range). The high spatial variability of R. alba at Cors Fochno may account for the difference between the two studies.

The proportionate contribution of winter emissions to the total CH$_4$ emission budget for Cors Fochno (9.4%) was lower than that reported by Laine et al. (2007) for the Glencar blanket bog (c. 21.3%). However, given that the Glencar winter emissions estimates was for the November – April period - presumably to facilitate comparison with winter emission estimates reported by Alm et al. (1999) for the Salmisuo peatland - the 9.4% value reported for Cors Fochno is a more realistic estimate of the potential contribution of winter emissions to the annual CH$_4$ budgets of UK/Irish peatlands.

4.2.2 Spatial variations of CH$_4$ emissions

4.2.2.1 Importance of water table position

Average depth to water table was the best individual predictor of spatial variation in annual CH$_4$ emissions and mean CH$_4$ flux, predicting a third of the variation in emissions (SWR2a & 2b). Laine et al. (2007) reported a moderately strong exponential relationship between annually-averaged CH$_4$ fluxes and median depths to water table across the 21 microforms at Glencar ($r^2 = 0.43$, p < 0.05) while Dinsmore et al. (2009) did not find average water table depth to be a significant predictor of CH$_4$ fluxes averaged over the full study period (19 months). As noted in Section 2.4.2.1, water table position exerts an indirect control on CH$_4$ emissions by controlling the size of the oxidizing surface peat layer. Although it predicted a third of spatial variation between all 20 collars at Cors Fochno, average water table position was not a significant predictor of emissions variation between the lawns and hollows. An insignificant control of water table position on emissions between lawns and hollows could be attributed to the small variations in average water table position between the individual microforms (average water table positions range from 0 - 9.6 cm, n =15). Laine et al. (2007) reported a similar finding for “high” and “low” lawns at Glencar (average water table positions ranged from 2 - 7 cm). The Cors Fochno data suggests that factors other than water table position
may be more relevant for determining spatial variations in emissions between microforms of generally high water table. In future studies it would make sense to examine the importance of subsurface controls on emissions variations by collecting quantitative data on the chemical properties of the peat under lawns with similar surface vegetation composition and average water table position.

4.2.2.2 IMPORTANCE OF VEGETATION

As noted in Sections 2.3.1 and 2.4.2.3, the importance of sedges as predictors of spatial variation in emissions has been well documented for Canadian and Scandinavian peatlands (e.g. Bellisario et al., 1999; Bubier et al., 1995; Nilsson et al., 2001). As well as transporting CH$_4$ to the atmosphere, it is possible that sedges both stimulate CH$_4$ production and emissions by delivering substrate for methanogenesis to the rhizosphere (via root exudation) and suppress production by supplying O$_2$ to methanotrophs. At Cors Fochno, the abundance of Rhynchospora alba was a poor predictor of spatial variation between the 20 microforms. However, for mud-bottomed hollow and hummock microform-type groups, within-group differences in the abundance of R.alba explained most of the annual CH$_4$ emissions variation and in both groups emissions increased with increasing percentage cover of the sedge. As noted in Section 2.4.2.3, several authors have suggested a strong control of oxidation on emissions from hummocks (e.g. Bubier et al., 1993; Roulet et al., 1997). At Cors Fochno, the three hummocks with high percentage cover of R. alba (83-99%) had annual CH$_4$ emissions totals comparable to those from lawns and hollows with significantly higher average water table position. This demonstrates that, where present, sedges may be an important control on emissions from elevated hummock microforms. Whether the role of R. alba in CH$_4$ emissions reflects a strong transport- or production-control is unclear: it is possible that both were important. Future investigations at Cors Fochno could investigate the role of R. alba using pulse-chase labelling of the carbon in the CO$_2$ taken up by sedges to see whether it appears in the emitted CH$_4$. Such experiments would help constrain the role of sedge-mediated CH$_4$ production in emissions.

Although overall R. alba was a weak individual predictor of emissions variation, when the R.alba variable was combined with average water table or Sphagnum moss cover, 51% and 67-68% of spatial variation between all 20 collars was explained, respectively. Different Sphagnum mosses have been shown to be good
predictors of emissions variations due to their sensitivity to water table position (Bubier et al., 1995). In this research, all Sphagnum species were combined into one variable and only the mud-bottomed hollows and one sedge lawn were not entirely covered with moss. On the basis of multiple walkovers at the site during this research, small mud-bottomed hollows and patches of bare peat (often containing sedges) appeared to be widespread at Cors Fochno. However, Boogert (2009) estimated that mud-bottomed hollows represented a small fraction of the central dome surface (c. 4%). As noted in Section 3.5.4, there was some uncertainty in Boogert’s classification of the peat surface with respect to mud-bottomed hollows due to shadowing in the low-altitude aerial photographs. In future it would be useful to test the uncertainties associated with identifying these small features of the peatland surface more thoroughly. It would be useful also to ‘map’ a larger area of the peatland using kite-based photography so to evaluate the spatial extent of mud-bottomed hollows over the full peat dome. So doing would help to elucidate the suitability of a model based on R. alba and Sphagnum moss cover for scaling-up at Cors Fochno.

4.2.3 CONTROLS ON TEMPORAL VARIATIONS IN CH₄ FLUX

4.2.3.1 TEMPERATURE

CH₄ flux from each microform-type was related most strongly to temperature, with average air temperature during the week prior to the flux-chamber measurement the strongest individual abiotic predictor of CH₄ fluxes. However, given the strong correlation between air temperature and solar radiation, it is possible that the control of temperature per se was not as strong as indicated by the regressions (discussed further in next section). Temperature controls rates of CH₄ production, CH₄ oxidation and carbon turnover in near-surface peat where most of the CH₄ emitted from peatlands is produced (e.g. Clymo & Pearce, 1995). As noted in Section 2.5.1.1, there is evidence in the literature that CH₄ production shows a stronger temperature-dependence than CH₄ oxidation (Dunfield et al., 1993), with production increasing more than consumption per unit of temperature rise. As a result, one would expect emissions also to increase with temperature, provided transport processes are not inhibited. For all microform-types, emissions were generally highest in late summer and lowest in winter, with notable peaks in emissions also occurring during a warm spell in late spring (all microform-types except sedge lawns) and late winter (mud-bottomed hollows only). The general
seasonal pattern is consistent with that shown for both temperate and boreal peatlands (e.g. Laine et al., 2007; Saarnio et al., 1997).

Temperature was a relatively weak predictor of $\text{CH}_4$ fluxes from hummocks compared to lawns and hollows. It is possible that the difference between microform-types relates to a stronger control of oxidation over production in some of the hummocks (particularly hummocks with low cover of sedges). It is possible also that the difference relates to differences in thermal regime beneath the dry hummocks and relatively wet lawns and hollows (Section 2.4.2.2). Average temperatures at 20 cm depths below the peat surface were not significantly different between the microform-types. However, given that the 20 cm depth was often above the water table in hummocks, it is not known whether there were significant differences between temperatures in the anaerobic peat where $\text{CH}_4$ production occurs. In future it would make sense to measure peat temperatures continuously throughout the year at shallow depths below the water table of the different microform-types (e.g. Bubier et al., 1995). So doing may elucidate whether a difference in thermal regime could explain the relatively weak control of air temperature on emissions from hummocks.

4.2.3.2 SOLAR RADIATION, RAINFALL AND BAROMETRIC PRESSURE

Weekly-totalled solar radiation, weekly-averaged pressure and weekly- and daily-totalled rainfall were significant predictors in the main regression model (SWR3a), but explained only a small fraction of overall variation in $\text{CH}_4$ flux (collectively 6%). Of the three abiotic factors, fluxes were related most strongly to solar radiation and, as noted in the previous section, there was likely to be some overlap in the temporal variation explained by solar radiation and air temperature. Solar radiation predicted temporal variation in microform-types with high cover of R. alba (i.e. sedge and Sphagnum lawn models (SWR3b & d)) only, suggesting a link between seasonal changes in solar radiation and the role of sedges in $\text{CH}_4$ emissions. As noted in Section 2.5.1.2, one might expect the importance of sedges in emissions to show seasonal variation due to seasonal changes in rates of photosynthesis. During autumn and winter, the decline in $\text{CH}_4$ flux was linked more strongly to a reduction in solar radiation than air temperature. It is possible that shortening daylight hours reduced rates of sedge-mediated $\text{CH}_4$ production and transport during these months. Week-on-week, the importance of short term variations in solar radiation on sedge-mediated $\text{CH}_4$ production and transport is unclear. Given
the high cover of R. alba across Cors Fochno and the importance of the sedge in \( \text{CH}_4 \) emissions, future studies might want to combine pulse-chase labelling techniques with higher-resolution \( \text{CH}_4 \) flux measurements (e.g. each day) from lawn microforms. Such experiments would reveal how short-term variations of solar radiation (e.g. due to changes in cloud cover) affect temporal variations of \( \text{CH}_4 \) flux.

As noted in Section 2.5.1.4, rainfall patterns and individual rainstorm events can drive temporal variations in \( \text{CH}_4 \) flux by changing water table position (a control on near-surface peat temperature, \( \text{CH}_4 \) oxidation potential and, possibly, ebullition rates) and pore-water chemistry in near-surface peat. There was little evidence that water table fluctuations and rainfall events exerted an important control on week-to-week variations in \( \text{CH}_4 \) flux at Cors Fochno. Weekly rainfall totals showed large variations in all seasons, but this variation appears to have influenced \( \text{CH}_4 \) fluxes from hummocks, only. Given that the explanatory power of the hummock model was very small, it is unlikely that rainfall was an important control on temporal variations of emissions throughout the year.

The significance of a barometric pressure variable in the main regression model and the partial models for sedge lawns, Sphagnum lawns and mud-bottomed hollows may be an indication that ebullition was captured at some points during the year by the chambers. As noted in Section 2.5.1.3, ebullition has been measured using chambers during periods of falling pressure (e.g. Tokida et al., 2007) and given that flux-chamber measurements were taken in a range of pressure conditions it is certainly possible that some pressure-related ebullition fluxes were captured. Nevertheless, given the limitations of flux-chamber method for studying controls on ebullition and the low explanatory power of the pressure variable, no firm conclusions can be drawn. Funnel-traps were used to explore the abiotic controls on ebullition in the second year of the research at Cors Fochno. The results of the analysis are presented in Chapter 6.

4.2.4 Summary of key findings

Microform-type was not a significant predictor of spatial variation of \( \text{CH}_4 \) emissions at the annual timescale (\( p > 0.05 \)); mean \( \text{CH}_4 \) flux and annual \( \text{CH}_4 \) emissions from each microform-type were not significantly different. The
abundance of two key species – R. alba and Sphagnum moss - was most relevant for describing spatial variation across the 20 microforms, while between mud-bottomed hollows and hummocks most of the variation could be explained by differences in the abundance of R. alba, only. A combination of air temperature, rainfall, barometric pressure and solar radiation variables provided the 'best fit' model of week-to-week variation of CH$_4$ flux from the 20 microforms. However, there was a spatially-varied response by the different microform-types to changing meteorological conditions, possibly linked to differences in vegetation cover and thermal conductivity of the near-surface peat. Winter emissions represented a significant proportion of the annual CH$_4$ budget (c. 9.4%).
Chapter 5  METHANE EBULLITION FLUXES FROM MUD- BOTTOMED HOLL OWS AND S PHAGNUM LAWNS

As discussed in Section 3.3, between 7th May and 12th September 2009 inverted funnel- traps provided a continual record of CH$_4$ ebullition fluxes to the water table of mud-bottomed hollows and Sphagnum lawns. This chapter reports on the frequency and magnitude of CH$_4$ ebullition fluxes to the funnel- traps and tests for statistical differences between the two microform- types. It also estimates CH$_4$ ebullition to the atmosphere after taking into account the effect of methanotrophy. Specifically, this chapter tests the following hypotheses:

- **HYPOTHESIS 4**: CH$_4$ ebullition fluxes to the water table of mud-bottomed hollows are greater than to the water table of Sphagnum lawns.

- **HYPOTHESIS 5**: For most of the summer/early autumn season, CH$_4$ arriving at the water table via ebullition is oxidized before reaching the atmosphere.

Full details of experimental and analytical methods and calculations pertaining to this chapter are found in Sections 3.3 - 3.5. Briefly, bubble volume in the funnel-traps was measured weekly throughout the study period and converted into a weekly average flux (mL gas m$^{-2}$). Samples of trapped gas were extracted from each funnel on a monthly basis and analysed for CH$_4$ concentration. Using the CH$_4$ data, weekly bubble fluxes were converted into CH$_4$ ebullition fluxes (expressed in units of mg CH$_4$ m$^{-2}$ d$^{-1}$). In this chapter, **HYPOTHESIS 4** was tested by applying a Student’s t-test to seasonally-averaged CH$_4$ ebullition fluxes for each of the twenty-eight funnel-traps. **HYPOTHESIS 5** was tested using the CH$_4$ ebullition flux data from this study together with rates of potential CH$_4$ oxidation calculated by Hornibrook et al. (2009) for a nearby ombrotrophic raised bog, Cors Caron. A rationale for using the data of Hornibrook et al. (2009) is provided in Section 5.1.4.
5.1 RESULTS

Eleven funnel-traps were operational from 7th May (19 weeks), twenty-three from 14th May (17 weeks) and twenty-eight from 28th May (16 weeks). For each weekly measurement, the temperature and pressure of entrapped bubble gas was estimated from air temperature and barometric pressures records for Cors Fochno (Section 3.2.7). Data analysis was performed on fluxes measured between 4th June and 12th September only (i.e. for the period when all of the funnels were operational).

5.1.1 FREQUENCY DISTRIBUTION OF BUBBLE FLUXES

Weekly bubble fluxes ranged from -83 – 12505 mL gas m⁻² for mud-bottomed hollows (n = 206) and -42 – 42722 mL gas m⁻² for Sphagnum lawns (n = 208). Negative fluxes were within the margin of error for the funnel-trap method. The frequency distribution of bubble fluxes was similar for both microform-types (see Figure 22) – both were non-normal with a strong positive skew.

![Figure 22: Frequency distributions of Sphagnum lawn and mud-bottomed hollow bubble fluxes.](image-url)
For mud-bottomed hollows, median flux was 292 mL gas m$^{-2}$ and the 25th and 75th percentiles were 83 and 750 mL gas m$^{-2}$, respectively. For the Sphagnum lawns, median flux was 291 mL gas m$^{-2}$ and the 25th and 75th percentiles were 94 and 615 mL gas m$^{-2}$, respectively.

5.1.2 $\text{CH}_4$ Concentration of Bubble Samples

$\text{CH}_4$ concentrations in extracted bubble samples ranged from 2868 – 674142 ppm (<0.3 % – 67.4% $\text{CH}_4$). Mean bubble $\text{CH}_4$ concentration was 233472 ± 17783 (SE) ppm (23.3% ± 1.8% $\text{CH}_4$, n = 95). On average, bubble samples from mud-bottomed hollow funnel-traps contained less $\text{CH}_4$ that those from Sphagnum lawns (average bubble content 22.0 ± 27.1% $\text{CH}_4$ and 24.8 ± 23.3% $\text{CH}_4$, respectively), but the difference was not statistically significant ($p > 0.05$). Overall, $\text{CH}_4$ concentrations increased between June and August and decreased between August and September a typical temporal pattern for $\text{CH}_4$ production rates in near surface peat (Figure 23).

![Figure 23: CH$_4$ concentrations of bubble samples.](image)

Boxes show the interquartile range of monthly bubble concentrations, thick cross bars represent the group median and vertical lines show the range. On 08/06 and 04/07, one 12 mL sample was sampled from 16 funnel-traps. On 09/08 and 13/09, two samples were extracted from 26 and 27 funnel-traps, respectively.
Low bubble CH$_4$ concentrations were measured in all months presumably due to partial oxidation of bubble CH$_4$ during transit to the funnel-traps. The CH$_4$ concentration in trapped bubbles is likely to have been constantly changing throughout each month as a function of: (a) variation in the CH$_4$ concentration of bubbles arriving in the traps, and (b) movement of CH$_4$ between the trapped gas and the water below (both water in the funnel and pore water in the peat below the funnel opening). It is possible that there was some diffusion of CH$_4$ from the funnel-gas to the funnel-water (i.e. a reduction in the CH$_4$ content of the bubble-gas) at rates dependent on: (i) changes in the CH$_4$ concentration gradient at the bubble-gas/funnel-water boundary over time, (ii) the position of the water surface within the funnel-trap, which controls the size of the diffusive surface area and (iii) the temperature and pressure of the enclosed funnel-gas/water (discussed further in Section 5.2.2).

5.1.3 RELATIONSHIP BETWEEN BUBBLE FLUX AND CH$_4$ EBULLITION

To generalise the relationship between bubble flux and CH$_4$ ebullition flux for the two microform-types, values representing cumulative (time-integrated) seasonal bubble fluxes and seasonal CH$_4$ ebullition fluxes were calculated for each funnel-trap. These data were separated by microform-type, plotted, and analysed using linear regression (see Figure 24). The regression indicated a strong positive relationship for mud-bottomed hollows ($r^2 = 0.76$, $p < 0.05$; $n = 14$). Although significant, the relationship was weaker for Sphagnum lawns, with much more scatter ($r^2 = 0.15$, $p < 0.05$; $n = 14$). The relationship was weak due to consistently

![Figure 24: Relationships between cumulative bubble flux and CH$_4$ ebullition flux to the water table.](image-url)
low CH₄ concentrations in two funnel-traps - 14 and 17 (exclusion of the funnel-trap data improved the relationship significantly, Δr² = 0.69, p < 0.05).

5.1.4 CH₄ EBULLITION FLUXES TO INDIVIDUAL FUNNEL-TRAPS

CH₄ ebullition fluxes to the funnel-traps (which is assumed to be equivalent to bubble flux to the water table) ranged from -1.0 - 784.5 mg CH₄ m⁻² d⁻¹ (n = 414). The median flux was 5.2 mg CH₄ m⁻² d⁻¹, 25th percentile 0.5 mg CH₄ m⁻² d⁻¹ and 75th percentile 17.6 mg CH₄ m⁻² d⁻¹. All 28 funnel-traps captured CH₄ ebullition in at least one week during the 16 week season. However, most were dormant (i.e. showed no evidence of ebullition) in at least one week and several for prolonged periods (up to four weeks). Cumulative (time-integrated) seasonal CH₄ ebullition fluxes ranged from 18.8 - 9407.3 mg CH₄ m⁻² (16 week period). The median seasonal flux was 1277.9 mg CH₄ m⁻², 25th percentile 292.2 mg CH₄ m⁻² and 75th percentile 2881.4 mg CH₄ m⁻². Nine funnel-traps accounted for 76.6% of the total seasonal flux from all funnel-traps combined (total seasonal flux 55.8 g m⁻²) (see Figure 25). Two funnel-traps (15 and 22) accounted for 30.8% of the total seasonal flux. The seasonal fluxes for traps 15 and 22 were statistical outliers within each microform-type group (i.e. seasonal flux was >1.5*(interquartile range) (Figure 25)). Both were thus categorised as ‘hotspots’ of CH₄ ebullition.

![Figure 25: Spatial variability of seasonal CH₄ ebullition fluxes to water table.](image-url)
5.1.5 Hypothesis 4: \( \text{CH}_4 \) ebullition fluxes to the water table of mud-bottomed hollows are greater than to the water table of Sphagnum lawns

Over 16 weeks, mud-bottomed hollow funnel-traps captured 29.2 g m\(^{-2}\) of \( \text{CH}_4 \) compared with 26.6 g m\(^{-2}\) for Sphagnum lawns (c. 9% less). Mean seasonal \( \text{CH}_4 \) ebullition for the two microform-types was 2.1 ± 0.8 (SE) mg \( \text{CH}_4 \) m\(^{-2}\) (\( n = 14 \)) and 1.9 ± 0.6 mg \( \text{CH}_4 \) m\(^{-2}\) (\( n = 14 \)) for mud-bottomed hollows and Sphagnum lawns, respectively (Figure 26). To test the significance of this difference, a Student's t-test was performed on the log\(_{10}\)-transformed mean seasonal \( \text{CH}_4 \) ebullition flux data (\( n = 28 \)). Log\(_{10}\)-transformation was necessary to normalise the data once separated by microform-type. The t-test revealed that the difference between the two microform-types was not significant (\( p > 0.05 \)) and the hypothesis was thus rejected.

![Mean seasonal CH\(_4\) ebullition flux (mg CH\(_4\) m\(^{-2}\))](image)

**Figure 26**: Box-plot of mean seasonal \( \text{CH}_4 \) ebullition fluxes for each microform-type.

Boxes represent the interquartile range of the mean seasonal \( \text{CH}_4 \) ebullition data for each microform-type group (14 values per group) while thick horizontal lines represent the group median. Error bars represent the lowest and second-highest value in the group. The two outliers - funnel-traps 22 and 15 - are shown with circles.
5.1.6 **HYPOTHESIS 5**: **FOR MOST OF THE SUMMER/ EARLY AUTUMN SEASON, CH$_4$ ARRIVING AT THE WATER TABLE VIA EBUILLITION IS OXIDIZED BEFORE REACHING THE ATMOSPHERE**

The test of **HYPOTHESIS 5** was based on potential CH$_4$ oxidation rates for Cors Caron - the nearest expanse of pristine patterned raised bog to Cors Fochno - which has similar peat, chemistry and vegetation characteristics to Cors Fochno. The Cors Caron Nature Reserve (52°15’24” N, 03°34’44”W) is located c. 44.6 km away by road and the dominant vegetation species are Sphagnum spp., Common Heather Calluna vulgaris (L.) Hull, Purple Moor Grass Molinia caerulea (L.) Moench, and Deergrass Trichophorum cespitosum (L.) Hartman. At an altitude of c. 160 m above sea level (a.s.l.), Cors Caron generally experiences higher rainfall than Cors Fochno and slightly cooler air temperatures. Daily air temperature and precipitation records for the Swyddffynnnon Meteorological Office Met. Station adjacent to Cors Caron (52°16’19”N, 03°54’54”W, 168 m a.s.l.) give an average annual rainfall total of c. 1450 mm for the period 2000 – 2009 compared with c. 1220 mm per annum for Cors Fochno. Annually averaged maximum daily air temperatures were 13.3 ± 0.3 °C (± std. dev.) for Cors Fochno (Fron-dirion Met. Station, Tal-y-bont) and 12.8 ± 0.5 °C for Cors Caron (Swyddffynnon Met. Station). Seasonality of precipitation and daily maximum air temperatures at Cors Caron are shown in Figure 27.

![Figure 27: Mean monthly precipitation and mean daily maximum air temperatures at Cors Caron for the period 2000 – 2009. Bars and points represent the monthly means while error bars represent the standard deviation.](image-url)
The present study was comparable to that of Hornibrook et al. (2009) in terms of: (i) peatland type and geographical location (both raised bog in West Wales), (ii) study period (both May – September), and (iii) choice of study sites within the peatland (the Cors Fochno Sphagnum lawns were similar to the two sites investigated by Hornibrook et al. (2009)). During the time periods of the ebullition study at Cors Fochno (May – September 2009) and the work conducted by Hornibrook et al. (2009) (May – September 2003), there were small differences (0.6 – 1.8°C) in the monthly-averaged daily maximum air temperatures at Cors Fochno and Cors Caron (Table 13). However, the seasonally-averaged (May – September) daily maximum air temperatures for Cors Caron and Cors Fochno were relatively similar. There was a notable difference in precipitation at the two sites during the two studies. Between July and September 2009, a high number of Atlantic low depressions across West Wales brought high rainfall and monthly precipitation totals were considerably higher than during the same period in 2003. As noted in

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>131.1</td>
<td>53.2</td>
<td>123.2</td>
<td>32.5</td>
<td>56.0</td>
</tr>
<tr>
<td>2009</td>
<td>94.8</td>
<td>36.3</td>
<td>177.2</td>
<td>74.1</td>
<td>69.7</td>
</tr>
</tbody>
</table>

Section 2.1.2, rates of CH₄ oxidation in peat are limited by O₂ and CH₄ availability, the latter of which is controlled by rates of CH₄ production (Segers, 1998). By raising water table position, high rainfall may increase rates of CH₄ production and decrease CH₄ oxidation by changing the relative extent of the anaerobic and aerobic zones in near-surface peat, respectively. Conversely, high rainfall may inhibit CH₄ production and increase CH₄ oxidation by introducing electron acceptors NO₃⁻, SO₄²⁻ and O₂ into near-surface peat (Section 2.5.1.4). It is not possible to know whether the high rainfall in 2009 would have resulted in significantly different estimates of CH₄ oxidation rates for Cors Caron than those estimated for 2003 by Hornibrook et

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>15.1</td>
<td>20.6</td>
<td>20.3</td>
<td>21.5</td>
<td>17.7</td>
</tr>
<tr>
<td>2009</td>
<td>15.3</td>
<td>20.1</td>
<td>19.4</td>
<td>19.1</td>
<td>16.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>337.4</td>
<td>46.9</td>
<td>105.8</td>
<td>27.7</td>
<td>38.3</td>
</tr>
<tr>
<td>2009</td>
<td>529.8</td>
<td>143.6</td>
<td>206.9</td>
<td>65.3</td>
<td>64.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>18.0</td>
<td>18.6</td>
<td>19.4</td>
<td>20.9</td>
<td>17.4</td>
</tr>
<tr>
<td>2009</td>
<td>17.2</td>
<td>18.5</td>
<td>18.3</td>
<td>18.2</td>
<td>16.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>3.1</td>
<td>2.3</td>
<td>3.8</td>
<td>3.6</td>
<td>3.3</td>
</tr>
<tr>
<td>2009</td>
<td>2.7</td>
<td>4.0</td>
<td>3.0</td>
<td>1.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>3.3</td>
<td>1.5</td>
<td>3.0</td>
<td>1.5</td>
<td>3.3</td>
</tr>
<tr>
<td>2009</td>
<td>3.3</td>
<td>4.0</td>
<td>3.0</td>
<td>1.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>13.8</td>
<td>18.6</td>
<td>19.4</td>
<td>20.9</td>
<td>17.4</td>
</tr>
<tr>
<td>2009</td>
<td>18.0</td>
<td>18.5</td>
<td>18.3</td>
<td>18.2</td>
<td>16.4</td>
</tr>
</tbody>
</table>
al. (2009). However, on the basis that: (i) \( \text{CH}_4 \) production (controlling \( \text{CH}_4 \) availability) is a strongly temperature-dependent process (Dunfield et al., 1995) and air temperatures were similar at Cors Caron and Cors Fochno between May - September 2003 and May - September 2009; (ii) between March 2008 and March 2009 air temperature was a stronger control on temporal variations in \( \text{CH}_4 \) flux at Cors Fochno than rainfall (Chapter 4); and (iii) the physical similarities (location, peatland type, vegetation) between Cors Fochno and Cors Caron, the \( \text{CH}_4 \) oxidation rates calculated by Hornibrook et al. (2009) for Cors Caron in 2003 were deemed to be a reasonable approximation for oxidation rates at Cors Fochno during the 2009 ebullition study.

Oxidation potentials for Cors Caron were calculated by Hornibrook et al. (2009) from laboratory analysis of \( \text{CH}_4 \) uptake kinetics in two surface peat cores and monthly field measurements of pore water \( \text{CH}_4 \) concentrations at two sites in raised bog. Rates of potential methanotrophy were measured for a 3 cm thick zone of near-surface Sphagnum peat (Table 14).

<table>
<thead>
<tr>
<th>Month</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>June</td>
<td>34.5</td>
<td>35.6</td>
<td>35.1</td>
</tr>
<tr>
<td>July</td>
<td>5.3</td>
<td>15.1</td>
<td>10.2</td>
</tr>
<tr>
<td>August</td>
<td>32.3</td>
<td>34.9</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Table 14: Rates of potential \( \text{CH}_4 \) oxidation.

Before applying the oxidation potentials to the Cors Fochno ebullition data, three assumptions were made: (i) a 3 cm thick zone of potential methanotrophy was also appropriate for the Sphagnum lawns across Cors Fochno, (ii) for mud-bottomed hollows – which were generally ponded but occasionally dry - a shallower zone of potential methanotrophy (1 cm thick) was more realistic, and (iii) none of the ebullition fluxes to the water table would have bypassed the methanotrophic zone. With respect to (i), a 3 cm thick zone was considered a reasonable ‘best estimate’ given the shallow zone of oscillating water table position (where most \( \text{CH}_4 \) oxidation occurs (e.g. Clymo & Pearce, 1995)) in Sphagnum lawns during spring and summer. With respect to (iii), given that the proportion of bubble fluxes that
bypassed the methanotrophic zone could not be determined from the weekly bubble flux measurements, an assumption that all CH₄ ebullition was depleted by methanotrophic processing above the water table would produce the most conservative estimate of potential CH₄ flux to the atmosphere via ebullition.

5.1.6.1 Calculating the effect of CH₄ oxidation on ebullition fluxes

The relevant oxidation rates for Cors Caron were subtracted from the average daily rate of CH₄ ebullition for the Sphagnum lawns for each funnel (Table 15). Hornibrook et al. (2009) did not measure oxidation rates in September, so the August average oxidation rate was used for CH₄ ebullition data from 01/08 – 12/09. Only 43 of the 208 daily average rates of CH₄ ebullition were greater than the potential rates of CH₄ oxidation, suggesting that 79% of average daily rates of CH₄ ebullition to the water table would have been entirely oxidized before reaching the atmosphere. For the mud-bottomed hollows, the average monthly oxidation rates for Cors Caron were first divided by three to reflect the shallower methanotrophic zone (see Table 15 for values), and 59% (121 out of 206) of the daily average CH₄ ebullition fluxes to the water table would have been entirely oxidized. A large difference between the microform types could be expected given the smaller potential for methanotrophy within mud-bottomed hollows compared to Sphagnum lawns.

5.1.7 Seasonal CH₄ ebullition flux to the atmosphere

To evaluate the potential importance of methanotrophic oxidation each week, total CH₄ ebullition to the water table (the sum of the weekly fluxes to each funnel-trap, mg m⁻²) was compared to estimated CH₄ ebullition to the atmosphere for each week during the season. After accounting for oxidation potentials, it was estimated that CH₄ was emitted to the atmosphere in all but one week of the season. In 5 of the 16 weeks (i.e. for 31% of the time), most CH₄ arriving at the water table was oxidized to CO₂ before reaching the atmosphere (in one week CH₄ was entirely oxidized, Table 16). In 11 of the 16 weeks (i.e. for 69% of the time), most of the CH₄ arriving at the water table escaped to the atmosphere.
### Table 15: Effect of methanotrophy on average daily rates of CH₄ ebullition.

<table>
<thead>
<tr>
<th>Time period</th>
<th>Range</th>
<th>n</th>
<th>Rate of potential CH₄ oxidation a (mg CH₄ m⁻² d⁻¹)</th>
<th>No. CH₄ fluxes entirely oxidized in 3 cm zone</th>
<th>No. CH₄ fluxes partially oxidized in 3 cm zone</th>
<th>Range of CH₄ fluxes that reached the atmosphere b (mg CH₄ m⁻² d⁻¹)</th>
<th>Average CH₄ flux to atmosphere (mg CH₄ m⁻² d⁻¹)</th>
<th>Average daily rates of CH₄ ebullition to water table (mg CH₄ m⁻² d⁻¹)</th>
<th>n</th>
<th>Range</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>28/05 to 30/06</td>
<td>-1.0 - 28.2</td>
<td>56</td>
<td>35.1</td>
<td>56</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-0.2 - 28.0</td>
<td>54</td>
<td>11.7</td>
<td>46</td>
</tr>
<tr>
<td>01/07 to 31/07</td>
<td>0 - 146.1</td>
<td>68</td>
<td>10.2</td>
<td>36</td>
<td>32</td>
<td>0.3 - 135.9</td>
<td>17.9</td>
<td>0 - 144.9</td>
<td>68</td>
<td>3.4</td>
<td>27</td>
</tr>
<tr>
<td>01/08 to 12/09</td>
<td>-1.0 - 784.5</td>
<td>84</td>
<td>33.6</td>
<td>73</td>
<td>11</td>
<td>3.1 - 750.9</td>
<td>103.4</td>
<td>-0.7 - 273.6</td>
<td>84</td>
<td>11.2</td>
<td>48</td>
</tr>
</tbody>
</table>

*Based on the average of two potential CH₄ oxidation rates calculated by Hornibrook et al. (2009) for June, July and August 2003. After dividing oxidation potentials shown for Sphagnum lawns by three to account for a 1 cm methanotrophic zone. This range accounts for partial oxidation in the methanotrophic zone.

### Table 16: Effect of methanotrophy on weekly-totalled CH₄ ebullition.

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Start</th>
<th>End</th>
<th>CH₄ ebullition to water table (mg m⁻²)</th>
<th>CH₄ loss to atmosphere (mg m⁻²)</th>
<th>% of CH₄ ebullition to water table oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>28- May</td>
<td>04- Jun</td>
<td>04- Jun</td>
<td>611.3</td>
<td>32.3</td>
<td>94.7</td>
</tr>
<tr>
<td>04- Jun</td>
<td>11- Jun</td>
<td>11- Jun</td>
<td>465.1</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>11- Jun</td>
<td>18- Jun</td>
<td>18- Jun</td>
<td>1287.5</td>
<td>215.5</td>
<td>83.3</td>
</tr>
<tr>
<td>18- Jun</td>
<td>25- Jun</td>
<td>25- Jun</td>
<td>1530.0</td>
<td>286.4</td>
<td>81.3</td>
</tr>
<tr>
<td>25- Jun</td>
<td>02- Jul</td>
<td>02- Jul</td>
<td>5767.3</td>
<td>4628.7</td>
<td>19.7</td>
</tr>
<tr>
<td>02- Jul</td>
<td>09- Jul</td>
<td>09- Jul</td>
<td>4003.8</td>
<td>3259.4</td>
<td>18.6</td>
</tr>
<tr>
<td>09- Jul</td>
<td>16- Jul</td>
<td>16- Jul</td>
<td>2762.0</td>
<td>2077.6</td>
<td>24.8</td>
</tr>
<tr>
<td>16- Jul</td>
<td>23- Jul</td>
<td>23- Jul</td>
<td>2558.5</td>
<td>1712.9</td>
<td>33.0</td>
</tr>
<tr>
<td>23- Jul</td>
<td>29- Jul</td>
<td>29- Jul</td>
<td>1632.0</td>
<td>1056.1</td>
<td>35.3</td>
</tr>
<tr>
<td>29- Jul</td>
<td>08- Aug</td>
<td>08- Aug</td>
<td>7746.1</td>
<td>4868.3</td>
<td>37.2</td>
</tr>
<tr>
<td>08- Aug</td>
<td>13- Aug</td>
<td>13- Aug</td>
<td>2642.8</td>
<td>1653.2</td>
<td>37.4</td>
</tr>
<tr>
<td>13- Aug</td>
<td>20- Aug</td>
<td>20- Aug</td>
<td>5620.9</td>
<td>3646.0</td>
<td>35.1</td>
</tr>
<tr>
<td>20- Aug</td>
<td>27- Aug</td>
<td>27- Aug</td>
<td>2213.6</td>
<td>723.3</td>
<td>67.3</td>
</tr>
<tr>
<td>27- Aug</td>
<td>03- Sep</td>
<td>03- Sep</td>
<td>4076.1</td>
<td>2473.0</td>
<td>39.3</td>
</tr>
<tr>
<td>03- Sep</td>
<td>12- Sep</td>
<td>12- Sep</td>
<td>12903.9</td>
<td>10288.1</td>
<td>20.3</td>
</tr>
</tbody>
</table>
To evaluate the importance of oxidation at the seasonal scale, cumulative (time-integrated) seasonal CH$_4$ fluxes to the atmosphere were calculated for each of the 28 funnel-traps (16 week period, expressed in units of g m$^{-2}$). A Student’s t-test on these fluxes revealed no significant difference between the microform-types ($p > 0.05$). From the 14 mud-bottomed hollows, the total seasonal CH$_4$ flux to the atmosphere was estimated to be 22.77 g m$^{-2}$ (22.1% less than the total seasonal ebullition flux to the water table). From the 14 Sphagnum lawns, the total seasonal ebullition flux was 14.15 g m$^{-2}$ (46.7% less than the total seasonal ebullition flux to the water table). Overall, 36.92 g CH$_4$ m$^{-2}$ were estimated to have been lost to the atmosphere during the season compared with seasonal flux to the water table of 55.82 g CH$_4$ m$^{-2}$ (Table 17). This suggests that methanotrophy may have oxidized only 33.9% of the CH$_4$ trapped by the funnels before it reached the atmosphere. Thus, at a seasonal scale most CH$_4$ arriving at the water table via ebullition would have reached the atmosphere.

Table 17: Seasonal CH$_4$ ebullition to the water table and atmosphere.

<table>
<thead>
<tr>
<th>Microform type</th>
<th>No. of funnel-traps</th>
<th>Mean seasonal CH$_4$ ebullition flux (g m$^{-2}$)</th>
<th>Total seasonal CH$_4$ ebullition flux$^a$ (g m$^{-2}$)</th>
<th>Mean seasonal CH$_4$ flux after oxidation losses (g m$^{-2}$)</th>
<th>Total seasonal CH$_4$ flux after oxidation losses$^a$ (g m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mud-bottomed hollow</td>
<td>14</td>
<td>2.09 (0.75)</td>
<td>29.24</td>
<td>1.63 (0.68)</td>
<td>22.77</td>
</tr>
<tr>
<td>Sphagnum lawn</td>
<td>14</td>
<td>1.90 (0.55)</td>
<td>26.58</td>
<td>1.01 (0.47)</td>
<td>14.15</td>
</tr>
<tr>
<td>Both</td>
<td>28</td>
<td>1.99 (0.45)</td>
<td>55.82</td>
<td>1.32 (0.41)</td>
<td>36.92</td>
</tr>
</tbody>
</table>

SE of means shown in brackets.

$^a$ The sum of cumulative (time-integrated) seasonal fluxes for each funnel-trap.

5.1.7.1 Seasonal Importance of Ebullition as a Transport Mechanism for CH$_4$

To assess the importance of the seasonal ebullition flux, it was useful to compare the average of the seasonal CH$_4$ ebullition fluxes to the funnel-traps (2009), to seasonal CH$_4$ emissions measured using chambers for the same period in 2008. For this analysis, cumulative (time-integrated) seasonal CH$_4$ emissions were calculated for five Sphagnum lawns and five mud-bottomed hollows (same 16-week period, expressed in units of g m$^{-2}$) from the 2008 chamber-flux data (reported in Chapter 4). These values represented seasonal CH$_4$ emissions via molecular diffusion, plant-transport and ebullition. Average cumulative CH$_4$ emissions from the chambers for 2008 were $6.14 \pm 1.56$ (SE) g m$^{-2}$ for Sphagnum lawns and $8.88 \pm 2.41$ g m$^{-2}$ for mud-bottomed hollows. Direct comparison with the average
seasonal CH₄ ebullition fluxes (Table 17) assumes that: (i) CH₄ emissions from Sphagnum lawns and mud-bottomed hollows during the 2009 season were similar to those during the same period in 2008 (i.e. inter-annual variability in CH₄ emissions was minimal), (ii) the microforms installed with funnel-traps were comparable to those used in 2008 and (iii) chambers captured emissions via molecular diffusion, plant-mediated transport and ebullition. On this basis, comparing seasonal averages (including standard errors) suggests that ebullition may have accounted for 8 - 36% of the CH₄ emissions from mud-bottomed hollows and 7 - 32% of the CH₄ emissions from Sphagnum lawns in the 2008 season. These values suggest that ebullition may be an important transport mechanism of CH₄ flux from Cors Fochno during summer months. However, given the prior assumptions, further work is required to test this hypothesis properly (see Discussion in Section 5.2.6).

5.2 DISCUSSION

5.2.1 SIZE AND FREQUENCY OF BUBBLE FLUXES
As noted in Chapter 2, the frequency of large-scale ebullition events across temperate and boreal peatlands (particularly those in regions experiencing climate warming) is unclear and produces uncertainty in peatland CH₄ budgets. The frequency distribution of bubble fluxes (measured weekly) suggests that large ebullition events were infrequent across the Cors Fochno peat dome. Most bubble fluxes were one or two orders of magnitude lower than those reported by Glaser et al. (2004) for the Lake Agassiz Peatland complex during three low pressure events (90000 – 120000 mL gas m⁻²). A distinctive characteristic of the Lake Agassiz peatland contributed to these large fluxes – i.e. the presence of a woody confining peat layer at c. 2 m depth which served to trap free-phase CH₄ (Glaser et al., 2004). Bubble fluxes reported here may represent the size and frequency of ebullition events for more typical peatlands (i.e. those without such characteristics). They also cover a more appropriate timescale for understanding ebullition dynamics than has been previously reported (i.e. a full summer/early autumn season compared with two or three days during low pressure events, e.g. Glaser et al., 2004; Tokida et al., 2007). The frequency distributions calculated here are the first to be reported for a patterned peatland. More ebullition data are required for a range of peatland types in order to evaluate fully the wider significance of the
frequency distributions. Of particular interest would be data measured at shorter timescales (e.g., every hour). This would illustrate the relative size and frequency of different types of ebullition flux (i.e. steady and episodic).

5.2.2 CH₄ CONCENTRATION OF BUBBLE SAMPLES

A constant CH₄ concentration value is often applied to bubble losses from peatland (e.g. Glaser et al., 2004; Rosenberry et al., 2003). However, as suggested by the Cors Fochno data, use of a constant value may be inappropriate and lead to inaccurate estimates of CH₄ emissions via ebullition. The CH₄ concentrations of bubbles arriving at the water table at Cors Fochno are highly variable - 0.3 – 67.4% CH₄ for mud-bottomed hollows (n = 48) and 3.6 – 64.3%CH₄ for Sphagnum lawns (n = 48). Given the novelty of the Cors Fochno research, there are no directly-comparable studies that investigate CH₄ concentrations. However, both ranges lie within that reported by Strack et al. (2005) for bubbles captured in funnel-traps below the surface of Sphagnum lawns in the St. Charles-de-Bellechasse poor fen (1.4 – 84%CH₄). The study by Strack et al. (2005) used funnels to measure the CH₄ concentration of bubbles within the peat profile, not fluxes to the water table per se. However, as at Cors Fochno, Strack et al. (2005) measured fluxes in Sphagnum lawns, recorded ebullition continually during summer and derived CH₄ concentrations from approximately monthly bubble sampling.

It was noted in Section 5.1.2 that one limitation of this research (and that of Strack et al. (2005)) is that low CH₄ concentrations may be partially a function of CH₄ oxidation within the funnel-trap and/or diffusion of bubble-gas CH₄ to the funnel-water over time (i.e. during the month between sampling). Direct sampling of in situ bubbles (i.e., those trapped within the peat profile) has demonstrated that bubble-gas concentrations can also be highly variable, with CH₄ concentrations reported of between <1% and c. 65% CH₄ (Tokida et al., 2007; Strack & Mireau, 2010). Thus, bubbles with a wide range of CH₄ concentrations can be expected to arrive at funnel-traps depending on their origin in the peat profile and their pathway to the funnel (Laing et al., 2008). However, to minimise the potential for bubble CH₄ depletion whilst in the funnel-traps, it is recommended that, in future, funnel-trap CH₄ concentration data are collected over shorter time intervals (days-weeks). Bubble fluxes to funnel-traps (in their current design) are sensitive to agitation by the observer/researcher. Thus, more frequent sampling would require an adaptation which allowed remote sampling (e.g. via c. 3 m tubing).
5.2.3 HOTSPOTS OF CH₄ EMBOLITON

The Cors Fochno research identified five locations that emitted negligible CH₄ to the atmosphere and two that were ‘hotspots’ of ebullition. Hotspots of CH₄ emissions have been identified previously in peatland pools and beaver ponds (Roulet et al., 1997; Strack et al., 2005), but the role of ebullition in terrestrial hotspots has not been clear. At Cors Fochno, one mud-bottomed hollow and one Sphagnum lawn were sites of high ebullition – representing 30.8% of the total seasonal CH₄ ebullition to the water table and 41.4% of total CH₄ emissions to the atmosphere. This demonstrates that it is possible for ebullition hotspots to occur in both aquatic and terrestrial peatland features. The factors that control the location of hotspots are not yet clear, but may be linked to structural properties of peat and the locations of zones of intense methanogenesis. From surface appearance, neither of the hotspots exhibited any particularly distinguishing features – both were typical of their ‘type’ in terms of topography and vegetation composition. In both cases, sedge roots were evident in the near surface peat below the funnel-traps. In future studies it would be interesting to test for significant differences in pore water CH₄ concentrations and peat structure between hotspots and sites of low ebullition.

The Cors Fochno data demonstrate high spatial variation within a small area of the wider peatland complex. A greater number of funnel-traps would have provided more robust statistical evidence for the frequency of hotspots across the bog dome. Yet, it is worth noting that even if funnel-traps were deployed in four times as many locations (an upper limit for one observer to install and monitor), their collective footprint would still represent a minute fraction of the peatland surface (5.49 m²). To increase the probability that important hotspots are accounted for in CH₄ budget estimates, the funnel-trap method may need to be supplemented with other techniques to identify sites of potentially high emissions (see Chapter 7).

5.2.4 SPATIAL VARIABILITY BETWEEN MICROFORM-TYPES

It was surprising to find no significant difference in seasonal CH₄ ebullition to the water table between the two microform-types and that differences in bubble CH₄ concentrations were also insignificant. Most mud-bottomed hollows across Cors Fochno formed part of larger lawn complexes and may have been formed quite recently. It is possible that, on average, the peat structure and chemistry of mud-
bottomed hollows was similar to that of Sphagnum lawns. However, visual inspection of peat immediately below the funnel-traps suggested distinct differences in peat structure between the microform-types – peat with von Post H scores of 8/9 in mud-bottomed hollows (sloppy, highly humified) and as low as 1/2 in Sphagnum lawns. The density of vascular plant roots also appeared to be generally lower for the mud-bottomed hollows compared to Sphagnum lawns. Without detailed information on peat chemistry and structure for the different microforms it makes little sense to speculate further. However, in future work it would make sense to collect reliable quantitative information on the chemical and physical properties of peat under the Cors Fochno lawns and mud-bottomed hollows.

5.2.5 Oxidation of CH₄ ebullition fluxes during transit between water table and atmosphere

Based on assumed rates of methanotrophic processing (Hornibrook et al., 2009) the weekly CH₄ ebullition flux to the water table was entirely consumed in only one of the 16 weeks. In 15 of the 16 weeks (i.e. 94% of the time) between 5 and 81% of the CH₄ trapped by the funnel-traps would have escaped to the atmosphere. On a seasonal basis, c. 22% of CH₄ was consumed between the water table and atmosphere in mud-bottomed hollows and c. 47% consumed in Sphagnum lawns. Given that the precise mechanisms for how bubbles move, coalesce and interact with oxidizing pore spaces are unclear it is not possible to gauge whether these absolute values reflect a true picture of CH₄ oxidation potential for bubbles moving between the water table and atmosphere. The range of CH₄ ebullition fluxes to the atmosphere (0.15 – 750.9 mg CH₄ m⁻² d⁻¹; n = 128) falls within that reported by previous authors (0 – 480 000 mg CH₄ m⁻² d⁻¹ – Baird et al., 2004; Glaser et al. 2003; Kellner et al., 2006; Comas & Slater, 2007; Rosenberry et al., 2003; Tokida et al., 2005 & 2007; Waddington et al., 2009). The seasonal flux to the atmosphere (36.9 g CH₄ m⁻²) is considerably higher than that reported by Strack et al. (2005) for the St. Charles-de-Bellechasse poor fen particularly given that Strack et al. (2005) did not account for potential methanotrophy. The number of sites investigated by Strack et al. (2005) was much lower than the 28 microforms used in this study and, as such, ‘hotter’ spots of CH₄ ebullition at their poor fen site may have been missed. The seasonal ebullition flux reported here is the ‘best estimate’ to date, but may still be conservative – i.e. more CH₄ may have reached the atmosphere.
than predicted by the estimate. It is likely that some of the ebullition fluxes were episodic in nature – moving at sufficient speed through the peat matrix to bypass zones of potential methanotrophy. It is also possible that the importance of CH$_4$ oxidation in mud-bottomed hollows was overestimated by assuming a 1 cm deep zone of methanotrophic processing. To test these hypotheses further using funnel-trap data, detailed information on the frequency of steady and episodic ebullition fluxes is required from future research. Rates of CH$_4$ oxidation potential in the near-surface of mud-bottomed hollows are also required – particularly for shallow hollows that experience prolonged periods of drought in summer months.

5.2.6 Relative importance of ebullition as transport pathway for atmospheric CH$_4$

As noted in Section 2.3.2, several authors have suggested that ebullition may be at least as important as plant-transport and diffusion as a mechanism of CH$_4$ loss from peatlands (e.g. Baird et al., 2004; Tokida et al., 2007). Based on the direct comparison of ebullition and total CH$_4$ flux data from 2008 (using chambers), the Cors Fochno research showed that ebullition may contribute a significant proportion of summer/early autumn CH$_4$ emissions from mud-bottomed hollows (c. 8 – 36%) and Sphagnum lawns (c. 7 – 32%). After continuous analysis of CH$_4$ fluxes from four Swedish Sphagnum peat cores over 30 – 60 days, Christensen et al. (2003) suggested a slightly higher and larger range (17%–50%) after quantifying episodic ebullition against a baseline of steady emissions (losses via plant-transport, diffusion and, presumably, steady ebullition) (see Section 2.3.2). Given the differences in methodology, results from the two studies are difficult to compare and it makes little sense to do so in any great detail.

The Cors Fochno estimates of CH$_4$ ebullition to the atmosphere are uncertain. However, they are the first for typical peatland microforms based on continual field measurements and form a benchmark for future studies. The Hornibrook et al. (2009) oxidation rates represented a ‘best estimate’ in the absence of empirical data for Cors Fochno. However, they did not pertain directly to mud-bottomed hollows or to oxidation of free-phase CH$_4$ and did not account for spatial variation in oxidation rates. To improve future estimates on the factors that control CH$_4$ ebullition from peatlands, more laboratory-based research is required on how methanotrophic processing effects bubble CH$_4$ concentrations within the highly
oxidizing pore spaces of near surface peat. Field and laboratory research similar to that of Hornibrook et al. (2009) is recommended – with a particular focus on the spatial variability of potential CH$_4$ oxidation rates for hollow and lawn microforms. Simultaneous measurements of plant-transport, ebullition and diffusion are also necessary to assess fully the importance of CH$_4$ ebullition as a mechanism of CH$_4$ loss to the atmosphere. Studies based on year-round field measurements are particularly important given that little is known about the magnitude and frequency of CH$_4$ ebullition fluxes outside spring and summer months.
Chapter 6  ABiotic Controls on Temporal Variation of Ebullition

This chapter evaluates the controls on temporal variability of ebullition during a 16-week summer/early-autumn season (28th May – 12th September 2009) and during two 55 – 68-hr low pressure events. Analysis is based on the weekly measurements of ebullition to 28 funnel-traps (Chapter 5) and rates of ebullition and CH$_4$ flux measured every 1.5 – 10 hr during the two low pressure events (using funnel-traps and flux-chambers). Specifically, the following hypothesis is tested:

- HYPOTHESIS 6: Air temperature, rainfall, wind speed and change in barometric pressure are important controls on ebullition. Of these, change in barometric pressure is the most important.

Methods pertaining to weekly bubble flux measurements have been described previously in Sections 3.3 - 3.5. In this chapter, weekly bubble flux data are expressed as average daily rates of ebullition (mL gas m$^{-2}$ d$^{-1}$) to facilitate comparison with previous research on the controls on ebullition. The methods used for high-frequency measurements during low pressure events are described in detail in Sections 3.2, 3.4 and 3.5. Briefly, between 3rd and 6th June 2009 (event 1) and 2nd and 4th September 2009 (event 2) bubble fluxes to funnel-traps were measured every 3 – 10 hr (expressed as an average hourly rate of ebullition, mL gas m$^{-2}$ h$^{-1}$) and CH$_4$ fluxes to two chambers every 1.5 – 8 hr (25 min period of operation, expressed in units of mg m$^{-2}$ h$^{-1}$). Twenty-six funnel-traps were operational during event 1 and 28 during event 2. CH$_4$ fluxes were measured from collars 19 and 20 – two mud-bottomed hollows with low cover of vascular vegetation and Sphagnum moss (see Section 4.1.4).

HYPOTHESIS 6 was tested using six stepwise multiple regression analyses on three separate datasets. The first and second regression analyses (SWR6a and SWR6b) were used to reveal the controls on temporal variation of ebullition to the water table over the full season. SWR6a (the main regression) was based on DATASET 1 which comprised bubble fluxes expressed as the average daily rates of ebullition to the 28 funnel-traps (one per funnel per week, n = 414) and 13 abiotic variables describing air temperature, wind speed, rainfall and changes in barometric pressure during the season. SWR6b was performed on DATASET 1 after separating
the data by funnel-trap ID (i.e. one regression per funnel-trap), enabling better understanding of the abiotic controls on ebullition within individual microforms.

The remaining four analyses (SWR6c-f) were used to reveal the controls on ebullition during the two passages of low barometric pressure (pressure events). The third and fourth regressions (SWR6c and SWR6d) were performed on Datasets which comprised the hourly rates of ebullition to the funnel-traps averaged for each measurement time (n = 18 for pressure event 1 and n = 13 for pressure event 2) and 10 abiotic variables describing changes in air temperature, wind speed, rainfall and barometric pressure during these events. The fifth and sixth analyses (SWR6e and SWR6f) were performed on Datasets which comprised 12 abiotic variables and CH$_4$ fluxes (mg CH$_4$ m$^{-2}$ h$^{-1}$) captured by the two chambers (one per chamber per measurement time; n = 40 for pressure event 1; n = 36 for pressure event 2). The flux-chamber measurements were used in SW6e and SWR6f so to determine the abiotic controls on CH$_4$ fluxes during the passages of low pressure systems.

6.1 RESULTS

6.1.1 VARIABILITY OF EMBULLITION RATES DURING SEASON

Average daily rates of ebullition ranged from 9.3 – 4746.9 mL gas m$^{-2}$ d$^{-1}$ (n = 414). The median rate was 41.7 mL gas m$^{-2}$ d$^{-1}$, the 25th percentile flux 11.9 mL gas m$^{-2}$ d$^{-1}$ and 75th percentile 93.8 mL gas m$^{-2}$ d$^{-1}$. Ebullition rates were generally higher during the second half of the season (Figure 28) and overall there was a weak but significant trend of increasing rates of ebullition as the season progressed (Spearman’s rank, $r_s = 0.17$, $p < 0.01$ (1-tailed), n = 414). One notable exception to the general trend was observed on 2nd July. Daily averaged air temperatures during the week of 25th June – 2nd July were relatively high (16.0 – 23.4°C; Cors Fochno AWS) (Figure 29a) and daily maximum temperatures (19.9 – 29.3°C) were in excess of the average daily max. temperatures for June 2000 – 2009 (17.4 ± 1.1°C; Fron-dirion (Tal-y-bont) Met. Station) (Section 3.1). Rainfall between 25th June – 2nd July was minimal (9.9 mm; Cors Fochno AWS) (Figure 29a).
Figure 28: Box plot of average daily rates of ebullition during the season.

Boxes represent the interquartile range of average daily rates of ebullition each week while the thick horizontal lines indicate the median. Bottom whiskers represent values in the lower quartile, while top whiskers represent those in the upper quartile which are not greater than 1.5*IQR. Values >1.5*IQR are outliers (circles) and values >3*IQR are extreme cases (asterisks).

6.1.2 METEOROLOGICAL CONDITIONS DURING SEASON

Daily temperatures (averaged over 24 hr) ranged from 10.3 – 18.7 °C in June, 12.7 – 23.4 °C in July, 12.1 – 19.8 °C in August and 7.8 – 17.1 °C in September (12 days only) (Cors Fochno AWS; Figures 29a). Due to an unseasonably high number of cold fronts, the average daily temperature was very similar in June, July and August - 14.7 ± 0.5 (SE) °C, 15.5 ± 0.4 °C and 15.0 ± 0.3 °C, respectively. Hourly averaged wind speeds during the season ranged from 0 – 23.2 mph and hourly rainfall intensity ranged from 0 – 6.5 mm h⁻¹ (Figure 29b). Total rainfall in June was 36.2 mm, 164.5 mm in July, 70.5 mm in August and 41.1 mm in September. The July 2009 rainfall total was extremely high compared to the previous two years.
(54.6 mm in 2007 and 60.1 mm in 2008) and high compared to the July average for 2000 - 2009 (108.5 mm; Fron-dirion Met. Station, Tal-y-bont). High rainfall accompanied the successive Atlantic low pressure systems that dominated July and August weather conditions.

Figures 29a & 29b: Air temperatures, rainfall totals, wind speeds and barometric pressures during season of ebullition measurements.
Due to the high number of Atlantic lows, average barometric pressure during the season was only 1008.7 hPa and for 25% of the season pressure was below 1002.8 hPa. Given that the magnitude and duration of pressure drops may be important controls on rates of ebullition, it was important to evaluate the range of pressure drops and their duration in each week of the season (Table 18). A drop in pressure was identified in the 2-hourly pressure log as a ≥ 1 hPa decline in pressure over at least four hours (e.g. time 00:00 - 1000.0 hPa, 02:00 - 999.5 hPa, 04:00 - 989.5 hPa; drop = 1.5 hPa, duration 4 hr). 44 drops in pressure were identified in the pressure record between 28th May and 12th September, occurring in all except one week. The magnitude of pressure drops ranged from 1.1 - 22.8 hPa, lasting 2 - 134 hr. The number, size and duration of individual pressure drops did not increase over time. However, pressure instability (indicated by the range or standard deviation of pressures each week) showed a general increasing trend with day of the season (Pearson correlations 0.69 and 0.65, p < 0.001, respectively). The increasing frequency of deep Atlantic lows was associated with the greater range in pressure as the season

Table 18: Summary of barometric pressure drops during season.

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Barometric pressure (hPa)</th>
<th>Pressure drops &gt; 1 hPa</th>
<th>Average daily rate of ebullition (mL gas m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>End a</td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>28-May 04-Jun</td>
<td>1014.1 - 1026.4</td>
<td>12.3</td>
<td>3.16</td>
</tr>
<tr>
<td>04-Jun 11-Jun</td>
<td>1003.9 - 1017.2</td>
<td>13.3</td>
<td>2.70</td>
</tr>
<tr>
<td>11-Jun 18-Jun</td>
<td>1009.3 - 1023.7</td>
<td>14.4</td>
<td>4.03</td>
</tr>
<tr>
<td>18-Jun 25-Jun</td>
<td>1005.5 - 1016.9</td>
<td>11.4</td>
<td>3.36</td>
</tr>
<tr>
<td>02-Jul 09-Jul</td>
<td>994.1 - 1011.7</td>
<td>17.6</td>
<td>5.05</td>
</tr>
<tr>
<td>09-Jul 16-Jul</td>
<td>994.8 - 1012.0</td>
<td>17.2</td>
<td>5.62</td>
</tr>
<tr>
<td>16-Jul 23-Jul</td>
<td>988.9 - 1011.1</td>
<td>22.2</td>
<td>6.19</td>
</tr>
<tr>
<td>23-Jul 29-Jul</td>
<td>995.1 - 1016.1</td>
<td>21.0</td>
<td>5.10</td>
</tr>
<tr>
<td>29-Jul 08-Aug</td>
<td>998.9 - 1017.3</td>
<td>18.4</td>
<td>5.52</td>
</tr>
<tr>
<td>08-Aug 13-Aug</td>
<td>1005.4 - 1016.8</td>
<td>11.4</td>
<td>3.07</td>
</tr>
<tr>
<td>13-Aug 20-Aug</td>
<td>996.6 - 1014.4</td>
<td>17.8</td>
<td>3.82</td>
</tr>
<tr>
<td>20-Aug 27-Aug</td>
<td>993.3 - 1016.2</td>
<td>22.9</td>
<td>6.40</td>
</tr>
<tr>
<td>27-Aug 03-Sep</td>
<td>982.5 - 1015.2</td>
<td>32.7</td>
<td>8.04</td>
</tr>
<tr>
<td>03-Sep 12-Sep</td>
<td>994.2 - 1034.1</td>
<td>39.9</td>
<td>11.67</td>
</tr>
</tbody>
</table>

a This is the date of weekly bubble flux measurement. Measurements taken between 11:00 and 12:00.
b Based on 2hr-averages measured with the continuous logging device between 12:00 GMT on start date and 12:00 on end date.
c Over a minimum of 4 hr.
d Total period of falling barometric pressure.
progressed. Ebullition measurements were recorded frequently (every 3 – 10 hr) during the second largest pressure drop of the season (during week 28- May – 04-Jun, pressure event 1) and during a near- average sized pressure drop (week 27-Aug – 03- Sept, pressure event 2).

6.1.3 LOW PRESSURE EVENTS
The first instrumented low pressure event (16:00 3rd June to 11:00 6th June) was associated with a cold front arriving from the Atlantic. Daily air temperatures were below the June average (13.2, 13.3, 11.8 and 10.8°C, for 3rd, 4th, 5th and 6th June, respectively) and hourly-averaged air temperature showed a strong diurnal signal on each day. During the event, barometric pressure rose from 1014.9 hPa to 1015.7 hPa before dropping 20.5 hPa over 50 hr. Rainfall was negligible (0.4 mm total) and winds were typically light to gentle (Figure 30a).

During event 2 (07:00 2nd Sept to 13:00 4th Sept) the pressure dropped 9.7 hPa during the first 24 hrs, and then rebounded to a final pressure of 1003.4 hPa (Figure 30b). Daily air temperatures were slightly cooler than during pressure event 1 (11.9, 13.0 and 12.4°C, for 2nd, 3rd and 4th September, respectively) and the diurnal air temperature signal was much weaker. Rainfall was considerably higher than for event 1, with 19 mm of rain falling during the 24 hr drop in pressure, and a further 3 mm during the pressure rebound. Winds were stronger and more variable than during event 1. Hourly averaged wind speeds ranged from 5 – 23 mph and were very strong during the first half of the pressure rebound.

6.1.3.1 TEMPORAL VARIABILITY OF EBUILLITON (DATASET 2)
Ebullition rates ranged from -1 – 6 mL gas m⁻² h⁻¹ (n = 468) during event 1 and -2 – 37 mL gas m⁻² h⁻¹ (n = 364) during event 2. Negative rates were within the margin of error for the method. Mean average hourly rates of ebullition ranged from 0 to 1 mL gas m⁻² h⁻¹ (n = 18) and 0 – 2 mL gas m⁻² h⁻¹ (n = 13), respectively. Rates of ebullition during phases of falling pressure were -1– 6 mL gas m⁻² h⁻¹ (n = 338) for event 1 and -2 – 19 mL gas m⁻² h⁻¹ (n = 139) for event 2. Rates of ebullition during the pressure increase in event 2 ranged from -2 – 37 mL gas m⁻² h⁻¹ (n = 223). Ebullition was negligible for 71% of measurements during pressure event 1 compared to 59% for pressure event 2. The 75th percentile fluxes were 0.3 mL gas m⁻² h⁻¹ and 0.7 mL gas m⁻² h⁻¹, respectively. Average hourly rates of ebullition varied between the funnel-traps during both events, but spatial variation was
Figures 30a & 30b: Mean hourly rates of ebullition to water table and \( \text{CH}_4 \) fluxes to atmosphere during low pressure events.
most pronounced during event 2, particularly during daylight hours (Figures 30a and 30b). Spikes in ebullition were evident at 12:30 and 12:45 pm on days 2 and 3 during event 1. The first spike during event 1 corresponded with the start of the pressure drop and the second when pressure had dropped to 1005 hPa. During event 2, there appeared to a strong diurnal pattern of mean ebullition on the second day of the event (discussed further in Section 6.2.2).

6.1.3.2 Temporal Variability of CH₄ Fluxes (Dataset 3)

CH₄ flux rates (derived from chamber-measurements) ranged from 0.8 – 8.1 mg CH₄ m⁻² h⁻¹ (n = 40) during event 1 and 0.3 – 13.9 mg CH₄ m⁻² h⁻¹ (n = 36) during event 2. After pressure dropped to 1011 hPa in event 1, a large spike in CH₄ flux was measured from collar 20 (a mud-bottomed hollow containing several Rhynchospora alba and Eriophorum spp. plants) and fluxes from both collars became highly variable (Figures 30a). During event 2, fluxes were generally less variable than during event 1 and there was a general trend of decreasing fluxes with time over the course of the event (Figures 30b). This decline was in contrast to general increases of wind speed, air temperature and, for the most of the event, barometric pressure. A large spike in CH₄ flux (13.9 mg CH₄ m⁻² h⁻¹) was measured from collar 19 (containing one Menyanthes trifoliata plant but no sedges) towards the nadir of the pressure drop. The flux coincided with a sharp drop in wind speed – from an hourly averaged speed of 11.9 mph at 20:00 to an hourly-average of 6.3 mph at 22:00 – and a period of intense rainfall. The flux was higher than any rate recorded previously during the one and half year study at Cors Fochno (maximum flux in 2008 was 190.1 mg CH m⁻² d⁻¹ or 7.9 mg CH₄ m⁻² h⁻¹) and is assumed to have been caused by ebullition.
6.1.4 HYPOTHESIS 6: AIR TEMPERATURE, RAINFALL, WIND SPEED AND CHANGE IN BAROMETRIC PRESSURE ARE IMPORTANT CONTROLS ON EBULLITION. OF THESE, CHANGE IN BAROMETRIC PRESSURE IS THE MOST IMPORTANT.

Two stepwise multiple regressions were used to test for significant abiotic controls on temporal variability during the season and four were used to test for significant controls during the two low pressure events. The abiotic variables used in the six analyses are shown in Table 19.

Table 19: Predictive variables used in stepwise regression models SWR6a – SWR6f.

<table>
<thead>
<tr>
<th>Environmental factor</th>
<th>Variable</th>
<th>Abbrev.</th>
<th>Variables used in each stepwise regression model (SWR) (indicated with an asterisk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barometric pressure (hPa)</td>
<td>At time of measurement</td>
<td>p</td>
<td>6a 6b 6c 6d 6e 6f</td>
</tr>
<tr>
<td></td>
<td>Min. during measurement interval</td>
<td>Pmin</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Range during measurement interval⁴</td>
<td>Prange</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Min. drop in pressure</td>
<td>Pmind</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Max. drop in pressure</td>
<td>Pmax</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Duration of max. drop in pressure (hr)</td>
<td>Pmaxdur</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Duration of all drops in pressure (hr)</td>
<td>Ptotaldur</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Change between measurements</td>
<td>ΔP</td>
<td>*</td>
</tr>
<tr>
<td>Air temperature (°C)</td>
<td>At time of measurement</td>
<td>T</td>
<td>⁶a ⁶b ⁶c ⁶d ⁶e ⁶f</td>
</tr>
<tr>
<td></td>
<td>Mean during measurement interval</td>
<td>Tmean</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Change between measurements</td>
<td>ΔT</td>
<td>*</td>
</tr>
<tr>
<td>Rainfall (mm)</td>
<td>Total on day prior to measurement</td>
<td>Rt-1</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Total during measurement interval</td>
<td>Rtotal</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Change between measurements</td>
<td>ΔR</td>
<td>*</td>
</tr>
<tr>
<td>Solar radiation (W m⁻²)</td>
<td>At time of measurement</td>
<td>S</td>
<td>⁶a ⁶b ⁶c ⁶d ⁶e ⁶f</td>
</tr>
<tr>
<td></td>
<td>Total during measurement interval</td>
<td>Stotal</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Change between measurements</td>
<td>ΔS</td>
<td>*</td>
</tr>
<tr>
<td>Wind speed (mph)</td>
<td>Speed at time of sampling</td>
<td>W</td>
<td>⁶a ⁶b ⁶c ⁶d ⁶e ⁶f</td>
</tr>
<tr>
<td></td>
<td>Mean during measurement interval</td>
<td>Wmean</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Change between measurements</td>
<td>ΔW</td>
<td>*</td>
</tr>
</tbody>
</table>

⁴ Range of pressure was very strongly correlated with the standard deviation of pressures each week (Pearson correlation 0.97 p < 0.001). Thus only one of the variables was included in the analysis as a measure of pressure stability.

The first stepwise regression analysis (SWR6a) was performed on the seasonal data (DATASET 1) - averaged daily rates of ebullition (one value per funnel-trap per week,
n = 414). Range of barometric pressures between measurements (an indicator of pressure stability) was the best predictor of variation in the data ($r^2 = 0.062$, $p < 0.001$), followed by mean wind speed in Step 2 ($\Delta r^2 = 0.023$, $p < 0.001$) and mean air temperature at the time of measurement in Step 3 ($\Delta r^2 = 0.02$, $p < 0.01$). Mean wind speed and mean air temperature variables were correlated with range in barometric pressure (Pearson correlations 0.67 and -0.59, $p < 0.001$, respectively) so it was not possible to determine exactly the proportion of variation each variable explained. Multicollinearity produced uncertainty in the multivariate regression models at Steps 2 and 3 (Step 2 average variance inflation factor (VIF) 1.86, Step 3 average VIF 1.86) (Table 20).

Table 20: Stepwise multiple regression on average daily rates of ebullition during season (SWR6a).

<table>
<thead>
<tr>
<th>Step</th>
<th>Predictor(s)</th>
<th>$r^2$</th>
<th>$p$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Range of barometric pressure during measurement interval, $P_{range}$</td>
<td>0.062*</td>
<td>&lt;0.001</td>
<td>425.1</td>
</tr>
<tr>
<td>2</td>
<td>$P_{range}$+ Mean wind speed during measurement interval, $W_{mean}$</td>
<td>0.085</td>
<td>&lt;0.001</td>
<td>420.4</td>
</tr>
<tr>
<td>3</td>
<td>$P_{range}$+ $W_{mean}$ + Mean temperature during measurement interval, $T_{mean}$</td>
<td>0.105</td>
<td>&lt;0.001</td>
<td>416.3</td>
</tr>
</tbody>
</table>

* denotes the $r^2$ of the ‘best fit’ model that was not compromised by co-varying factors

The main regression (SWR6a) was re-run after separating the data by funnel-trap (i.e. the regression analysis was run for each individual funnel-trap) to evaluate the significance of the abiotic variables at the microform-scale (SWR6b). Significant abiotic controls on temporal variation of ebullition were evident in 23 of the 28 funnel-trap models (Table 21). The importance of individual controls showed high spatial variation. All multivariate models indicated a significant degree of multicollinearity between variables (average VIF value >1.5). All four abiotic variables - air temperature, rainfall, wind speed and barometric pressure - were significant in just one model (funnel-trap 14). Air temperature was the most widely-important abiotic factor, with air temperature variables appearing in 18 of the models – in 13 of which it was the most significant abiotic factor. In each model where air temperature was the most important factor, the relationship between the air temperature variable and daily rates of ebullition was positive, suggesting that seasonal warming of near-surface and medium depth peat (c. 0 – 2 m depths) increased rates of ebullition in these microforms. Range of pressure was the most important of the pressure variables – the most significant variable in six of the funnel-trap models. Metrics describing periods of falling pressure were significant in only four models. Wind speed and rainfall appeared to be of lesser importance than barometric pressure and air temperature as drivers of ebullition.
Rainfall appeared in six models – in three of which it was the most significant abiotic factor. Wind speed appeared in four multivariate models with range of barometric pressure and one multivariate model with temperature and two of the pressure variables.

Table 21: Stepwise multiple regressions for individual funnel-traps.

<table>
<thead>
<tr>
<th>Funnel-trap</th>
<th>Predictor(s)</th>
<th>r²</th>
<th>p</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWR6b</td>
<td><strong>One significant variable</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Mean air temp. during measurement interval, ( T_{\text{mean}} )</td>
<td>0.39</td>
<td>&lt;0.05</td>
<td>7.2</td>
</tr>
<tr>
<td>4</td>
<td>Mean air temp. during measurement interval, ( T_{\text{mean}} )</td>
<td>0.66</td>
<td>&lt;0.001</td>
<td>76.4</td>
</tr>
<tr>
<td>7</td>
<td>Mean air temp. during measurement interval, ( T_{\text{mean}} )</td>
<td>0.54</td>
<td>&lt;0.01</td>
<td>31.6</td>
</tr>
<tr>
<td>12</td>
<td>Mean air temp. during measurement interval, ( T_{\text{mean}} )</td>
<td>0.28</td>
<td>&lt;0.05</td>
<td>17.6</td>
</tr>
<tr>
<td>27</td>
<td>Mean air temp. during measurement interval, ( T_{\text{mean}} )</td>
<td>0.48</td>
<td>&lt;0.01</td>
<td>19.7</td>
</tr>
<tr>
<td>9</td>
<td>Air temp at time of measurement, ( T )</td>
<td>0.27</td>
<td>&lt;0.05</td>
<td>69.7</td>
</tr>
<tr>
<td>28</td>
<td>Air temp at time of measurement, ( T )</td>
<td>0.61</td>
<td>&lt;0.001</td>
<td>15.4</td>
</tr>
<tr>
<td>24</td>
<td>Rainfall on day prior to measurement, ( R_{t-1} )</td>
<td>0.44</td>
<td>&lt;0.01</td>
<td>207.7</td>
</tr>
<tr>
<td><strong>Two significant variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>( T_{\text{mean}} ) + ( T )</td>
<td>0.85*</td>
<td>&lt;0.001</td>
<td>17.7</td>
</tr>
<tr>
<td>3</td>
<td>( T_{\text{mean}} ) + Duration of max. drop in pressure, ( P_{\text{maxd}} )</td>
<td>0.78*</td>
<td>&lt;0.001</td>
<td>21.4</td>
</tr>
<tr>
<td>11</td>
<td>( T_{\text{mean}} ) + ( P_{\text{min}} )</td>
<td>0.61*</td>
<td>&lt;0.01</td>
<td>60.0</td>
</tr>
<tr>
<td>16</td>
<td>Range of barometric pressures during measurement interval, ( P_{\text{range}} ) + ( T_{\text{mean}} )</td>
<td>0.64*</td>
<td>&lt;0.01</td>
<td>31.8</td>
</tr>
<tr>
<td>18</td>
<td>Total rainfall during measurement interval, ( R_{\text{total}} ) + ( T_{\text{mean}} )</td>
<td>0.77*</td>
<td>&lt;0.001</td>
<td>50.7</td>
</tr>
<tr>
<td>19</td>
<td>Rainfall on day prior to measurement, ( R_{t-1} ) + ( P )</td>
<td>0.60*</td>
<td>&lt;0.01</td>
<td>337.6</td>
</tr>
<tr>
<td>25</td>
<td>Duration of all drops in barometric pressure, ( P_{\text{totaldur}} ) + ( P_{\text{maxd}} )</td>
<td>0.66*</td>
<td>&lt;0.01</td>
<td>13.4</td>
</tr>
<tr>
<td><strong>Multiple significant variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( T_{\text{mean}} ) + Min. barometric pressure during measurement interval, ( P_{\text{min}} ) + Barometric pressure at time of measurement, ( P ) + Wind speed at time of measurement, ( W )</td>
<td>0.86*</td>
<td>&lt;0.01</td>
<td>29.5</td>
</tr>
<tr>
<td>21</td>
<td>( T ) + ( P_{\text{maxd}} ) + ( R_{\text{total}} )</td>
<td>0.77*</td>
<td>&lt;0.001</td>
<td>7.9</td>
</tr>
<tr>
<td>10</td>
<td>( T ) + ( P_{\text{totaldur}} ) + ( R_{\text{total}} )</td>
<td>0.87*</td>
<td>&lt;0.001</td>
<td>11.6</td>
</tr>
<tr>
<td>14</td>
<td>( P_{\text{range}} ) + ( W_{\text{mean}} ) + ( T_{\text{mean}} ) + ( R_{\text{total}} )</td>
<td>0.58*</td>
<td>&lt;0.01</td>
<td>856.9</td>
</tr>
<tr>
<td>15</td>
<td>( P_{\text{range}} ) + ( W_{\text{mean}} ) + ( P_{\text{min}} )</td>
<td>0.92*</td>
<td>&lt;0.001</td>
<td>386.0</td>
</tr>
<tr>
<td>17</td>
<td>( P_{\text{range}} ) + Barometric pressure at time of measurement, ( P ) + ( P_{\text{min}} )</td>
<td>0.91*</td>
<td>&lt;0.001</td>
<td>347.7</td>
</tr>
<tr>
<td>20</td>
<td>( P_{\text{range}} ) + ( W_{\text{mean}} ) + ( P_{\text{min}} ) + ( T_{\text{mean}} )</td>
<td>0.93*</td>
<td>&lt;0.001</td>
<td>119.2</td>
</tr>
<tr>
<td>26</td>
<td>( P_{\text{range}} ) + ( W_{\text{mean}} ) + ( T_{\text{mean}} )</td>
<td>0.91*</td>
<td>&lt;0.001</td>
<td>63.3</td>
</tr>
</tbody>
</table>

* denotes the \( r^2 \) of the ‘best fit’ model. All best fit models were compromised by significant multicollinearity.

6.1.4.1 Tests on the Pressure Event Ebullition Data (Dataset 2)

Two stepwise multiple regressions were used to test for significant abiotic controls on temporal variability during pressure event 1 and pressure event 2 (Dataset 2, SWR6c & 6d). The dependent variable in each case was mean average hourly rates
of ebullition (one value per measurement time - \( n = 40 \) event 1, \( n = 36 \) event 2) and the significance criterion for acceptance in the model was \( p \leq 0.05 \). Results of the regression analyses indicated that temperature was the only significant driver of variability in rates of mean rates of ebullition during both events (Table 22). Change in air temperature between measurements was important during event 1 and temperature at the time of sampling during event 2. Results from both analyses indicated that short-term fluctuations in air temperature were more important as drivers of ebullition than falling pressure (discussed further in Section 6.2.2).

Table 22: Stepwise multiple regressions on pressure event ebullition data (SWR6c & 6d)

<table>
<thead>
<tr>
<th>SWR6c</th>
<th>Predictor(s)</th>
<th>( r^2 )</th>
<th>( p )</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure event 1</td>
<td>Change in air temperature between measurements, ( \Delta T )</td>
<td>0.23</td>
<td>&lt;0.05</td>
<td>0.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SWR6d</th>
<th>Predictor(s)</th>
<th>( r^2 )</th>
<th>( p )</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure event 2</td>
<td>Air temperature at time of measurement, ( T )</td>
<td>0.74</td>
<td>&lt;0.001</td>
<td>0.28</td>
</tr>
</tbody>
</table>

6.1.4.2 Tests using the pressure event \( \text{CH}_4 \) flux data (DATASET 3)

Two additional regressions were used to analyse controls on the \( \text{CH}_4 \) flux data (DATASET 3). Abiotic variables used in SWR6c & 6d were used in both regressions along with two solar radiation variable due to the presence of \( \text{CH}_4 \)-transporting vascular plants in each collar. Unexpectedly, the regression on the data for pressure event 1 (SWR6e) demonstrated that none of the abiotic variables were predictors of temporal variation of \( \text{CH}_4 \) flux (\( p > 0.05 \)). During event 2, wind speed was the only significant predictor of mean \( \text{CH}_4 \) flux – explaining 31% of the variation over the 55 hr event (SWR6f, Table 23). Given that mean wind speed was identified as a significant control on ebullition in the main seasonal regression and four of the funnel-trap models, the significance of wind speed in this model is an

Table 23: Stepwise multiple regression on \( \text{CH}_4 \) flux data for pressure event 2 (SWR6f).

<table>
<thead>
<tr>
<th>SWR6f</th>
<th>Predictor</th>
<th>( r^2 )</th>
<th>( p )</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure event 2</td>
<td>Wind speed ( W )</td>
<td>0.31</td>
<td>&lt;0.001</td>
<td>2.00</td>
</tr>
</tbody>
</table>
indication that CH₄ ebullition was captured by the chambers during the event. As noted in Section 6.1.3, wind speeds were highly variable during the event, often changing rapidly between chamber measurements. Such changes in wind speed are indicative of air pressure changes (Section 2.5.1.4) which have the potential to cause widespread ebullition.

6.1.4.3 Summary of the individual test results with respect to Hypothesis 6

Acceptance of Hypothesis 6 required that there was clear evidence that (i) air temperature, wind speed, rainfall and changes in barometric pressure were important controls on ebullition and (ii) that change in barometric pressure was the most important abiotic control. Given the spatially-varied response to the abiotic factors and different responses at the different timescales, the hypothesis was partially (and tentatively) accepted as follows:

At the seasonal timescale the hypothesis was accepted with respect to air temperature and wind speed based on the analysis of the full ebullition dataset (SWR6a). At the microform-scale, the hypothesis was fully accepted for one Sphagnum lawn and fully rejected for the five microforms for which ebullition fluxes could not be modelled. Part (i) of the hypothesis was accepted on the basis that a minimum of 5 funnel-trap models indicated a significant response of ebullition to each of the abiotic factors (SWR6b). At the timescale of individual pressure events, part (i) of the hypothesis was rejected for range of pressure and rainfall, but accepted for air temperature (SWR6c & d) and wind speed (SWR6f).
6.2 DISCUSSION

6.2.1 COMPARING RATES OF EBULLITION

This research at Cors Fochno is the first to demonstrate the spatial and temporal variability of ebullition during a full summer season. As noted in Chapter 2 (section 2.3.2), several studies have employed funnels or other gas traps to capture bubble fluxes at/above the water table, but all have been limited by sample size. Strack et al. (2005) reported daily averaged rates of ebullition to one near-surface funnel-trap between May - September in the range of 38.2 – 712.9 mL gas m\(^{-2}\) d\(^{-1}\) (St. Charles-de-Bellechasse poor fen, Quebec). Baird et al. (2004) reported bubble fluxes from the surface of six Sphagnum peat cores incubated at a constant temperature of 12°C (a near-surface peat temperature measured in late spring, summer and early autumn) in the range of 0 – 88.9 mL gas m\(^{-2}\) d\(^{-1}\) (average daily rates) of ebullition, cores from Cors Fochno and Longbridgemuir peatland, Scotland). The range of ebullition fluxes reported by Strack et al. (2005) and Baird et al. (2004) is much smaller than the range measured at Cors Fochno (-9.3 – 4746.9 mL gas m\(^{-2}\) d\(^{-1}\), n = 414). This can be attributed partially to the small sample size employed by Strack et al. (2005) and Baird et al. (2004). As indicated by the research reported here for Cors Fochno, for estimates of ebullition potential to be reliable, future studies need to account for high spatial variation of ebullition across patterned peatlands.

This is the first field-based study to have measured ebullition directly during periods of falling pressure. Previous rates of ebullition measured in situ have been inferred from indirect measurements of subsurface gas fluctuations in response to changing pressure (e.g. Glaser et al., 2004; Rosenberry et al., 2003) and/or using chambers (e.g. Tokida et al., 2005, 2007) from which it is difficult to estimate the 'true' ebullition flux (Table 2, Section 2.3.2). Previously-reported rates of ebullition during falling pressure range from c. 0.1 – 13404.0 mL gas m\(^{-2}\) h\(^{-1}\) (e.g. Tokida et al., 2007; Rosenberry et al., 2003; Glaser et al., 2004) based on events lasting < 1 hr (Tokida et al., 2007) to several days (Rosenberry et al., 2003). Ebullition fluxes measured during falling pressure at Cors Fochno were at the low end of the reported range (~2.0 – 18.5 mL gas m\(^{-2}\) h\(^{-1}\), n = 477), but it is possible that larger fluxes in response to pressure drops occurred at Cors Fochno in areas not monitored by the funnels and/or at other times during the season (discussed further in Section 6.2.3). Differences in methodology and scale of investigation...
may explain the large variation in the rates reported. Large variation may also reflect a control of peat structure and peat quality on rates of bubble accumulation in different peat types. More research is needed on the subsurface factors that control the response of ebullition to falling pressure in order to evaluate fully its importance as a ‘trigger’ for widespread ebullition (discussed further in section 6.2.6).

6.2.2 CONTROL OF TEMPERATURE

Increasing air temperature was linked to increasing rates of ebullition in 18 microforms, suggesting a widespread control of temperature on bubble dynamics. Evident from the Cors Fochno data was an ebullition response to both pronounced increases in weekly-averaged air temperature and diurnal temperature fluctuations. For example, on 2\textsuperscript{nd} July, a large spike in ebullition was detected in 21 of the 28 funnel-traps in response to a period of unseasonably warm weather and low rainfall. Of the 18 funnel-trap models that identified air temperature as a significant control on ebullition, 17 corresponded to microforms which clearly showed a spike in ebullition on 2\textsuperscript{nd} July. With respect to diurnal temperature fluctuations, during both pressure events diurnal warming/cooling of near-surface peat appeared to be the significant driver of ebullition variation over the 55 – 68 hr periods, particularly during the second pressure event in early September.

The temperature-effect on ebullition is most likely a result of processes in the near-surface and medium-depth (0 – 2 m) peat, particularly the upward movement of bubbles in response to increased volume (Ideal Gas Law) and buoyancy and an increase in free-phase gas content due to (i) a decrease in gas solubility (encouraging the migration of gases from dissolved to free-phase, Henry’s law) and (ii) an increase in rates of gas production, particularly CH\textsubscript{4} (enhancing the potential for new bubbles to form and existing bubbles to grow). From the Cors Fochno data, it was not possible to gauge the relative importance of these processes on ebullition fluxes per se or to elucidate whether different processes were more important than others in different microforms and/or at different times during the season. Yet, the response of ebullition to diurnal fluctuations in air temperature is an important finding and more work is needed to evaluate the importance of diurnal variations in rates of ebullition. The effect of short-term temperature fluctuations on ebullition may be widespread across
patterned peatlands; particularly in microforms where water table is close to the peat surface and thermal conductivity is high (cf. Tokida et al., 2007). Testing on a range of peat types is important for understanding the wider significance of short-term peat warming as a driver of ebullition from northern peatlands.

6.2.3 CONTROL OF PRESSURE VARIATION

The main regression model (SWR6a) indicated that range of barometric pressures each week was the best predictor of ebullition rates during the season. However, it explained a small fraction of the variation in the data (6%) and when the data for each funnel-trap were analysed separately, ebullition in only six microforms showed a strong response to the range of barometric pressure each week. Five of the six microforms exhibited extremely large ebullition fluxes (844 – 4587.2 mL gas m⁻² h⁻¹, all in the highest 1% of rates measured during the season) in the final nine days of the season when pressure varied the most. Several authors have indicated that increases in bubble volume and buoyancy (e.g. Glaser et al., 2004) and increases in gas content during falling pressure are sufficient to drive ebullition fluxes of this magnitude (e.g. Tokida et al., 2007). It is not known whether it was falling pressure per se that drove the strong response of ebullition in these microforms because colinearity prevented further analysis of controlling factors. High wind speeds may also have been an important driver of ebullition (see Section 6.2.4). It is also possible that very low barometric pressures during the early stages of the final week enhanced ebullition in some microforms (minimum barometric pressure was significant in five funnel-trap models). There is some evidence from CH₄ fluxes measured during the second pressure event that episodic ebullition did occur in response to the sharp drop in pressure on 2nd September. Notwithstanding these possibilities, the most reliable conclusion from the seasonal data is that: (i) large changes in barometric pressure were important drivers of ebullition in some microforms, and (ii) very large ebullition fluxes (99th percentile) occurred during a period of large barometric pressure variation at the end of the season.

It is possible that strong response to pressure variation at the end of the season was due to the high gas content of the near-surface peat. Studies on near-surface peats have indicated that bubbles can build-up over several weeks and that increasing rates of CH₄ production (a highly temperature-dependent process)
contribute to a progressive increase in free-phase gas content (e.g. Kellner et al., 2004). In order to test this hypothesis, regular, simultaneous measurements of bubble ebullition and subsurface gas content during a full summer season are recommended in future peatland research. Non-invasive techniques using ground penetrating radar (e.g Comas & Slater, 2007; Strack & Mireau, 2010) may be particularly useful for establishing links between the volume of free-phase gas in different peatland microforms (in the near-surface and deep peat layers) and the response of ebullition to different size pressure variations.

6.2.4 CONTROL OF WIND SPEED

This is the first study to have demonstrated the potential importance of wind speed as a driver of ebullition. Mean wind speed appeared in four of the six funnel-trap models that indicated range of pressure was the strongest predictive variable. There was probably some overlap in the variation that range of pressure and wind speed explained (the variables were moderately strongly correlated, Pearson correlation 0.67, p < 0.001) so it is not possible to determine the 'true' importance of wind speed on ebullition rates during the season. It is possible that high wind speeds may have been responsible for some of the high rates of ebullition observed towards the end of season. As noted Section 2.5.1.4, high wind speeds may trigger episodic ebullition due to bubbles becoming dislodged in response to plants (and their roots) being agitated by the wind. Short-lived pressure variations as a result of wind gusts also have the potential to trigger ebullition. Both processes may have accounted for some of the CH₄ flux variation observed during the second pressure event. Both mud-bottomed hollows contained vascular plants - both within and outside the collar perimeter. Given that the roots of sedges grow both outwards (in multiple directions) and downwards, it is feasible that bubbles located around the roots of plants growing outside the collar perimeter were dislodged as the plants moved in the wind. In addition, short-lived pressure variations caused by wind gusts - translated to the flux-chamber via the pressure balloon - may have triggered ebullition fluxes during flux-chamber operation. Further work is needed to test these hypotheses. Specifically, laboratory-based investigations of the control of wind speed on ebullition in vegetated peat cores.
6.2.5 CONTROL OF RAINFALL

Rainfall was not a significant predictor of variation in the main regression model, but was significant within six of the funnel-trap models. High rainfall often accompanied low pressure systems and there was a strong inverse correlation between minimum barometric pressure and total rainfall during each measurement week (Pearson correlation -0.76, p < 0.001). Given the strong correlation, the significance of total weekly rainfall in several of the funnel-models may reflect a control of pressure rather than rainfall per se, particularly on rates of ebullition in the final weeks of the season. Rainfall may have exerted a more direct response on ebullition in some microforms earlier in the season. As noted in Section 2.5.1.4, rainfall can suppress rates of ebullition in peat by increasing hydrostatic pressure, causing free-phase gas to migrate back to dissolved phase and bubble volume (controlling the upward force of bubble buoyancy) to decrease. Reduction in hydrostatic pressure has been linked to ebullition during periods of drought and water table drawdown in some peatlands (e.g. Glaser et al., 2004; Treat et al., 2007). There was some evidence at Cors Fochno that water table drawdown contributed to spikes in ebullition observed in the first week of July. As noted previously (Section 6.2.2), increasing air temperature is likely to have been a strong control on the high rates of ebullition during this week. However, it is possible that a reduction in hydrostatic pressure enhanced rates of ebullition in some microforms.

6.2.6 SPATIALLY-VARIABLE RESPONSE OF EBULLITION TO ABIOTIC VARIABLES

The very weak best fit model ($r^2 = 0.10$, p < 0.001) of the full ebullition dataset (DATASET 1) was due largely to the spatial variability of ebullition and a spatially-varied response to the abiotic variables. The relative importance of air temperature, wind speed, rainfall and changes in barometric pressure varied widely between different microforms. This is an important finding in that it demonstrates that changes in temperature and barometric pressure (the most widely investigated abiotic controls) do not have a uniform effect on ebullition rates across patterned peatlands and that other abiotic factors may exert a significant control on ebullition. Mean air temperature between measurement weeks was the most widely-important predictor of temporal variation when the data for each microform were analysed separately (i.e. it was the most frequently observed variable in the funnel-trap models). Range of pressure was the next most
frequently observed variable followed by mean wind speed and total rainfall in the week prior to measurement.

It is possible that differences in peat structure (e.g. pore-size distribution and the presence/absence of impermeable strata or confining peat layers) and peat quality (which affects rates of gas production and consumption) (e.g. Baird et al., 2004; Strack & Mireau, 2010) explain the spatially-varied response of ebullition to the same meteorological conditions. However, without detailed information on differences in peat structures and subsurface gas dynamics during the season, this hypothesis cannot be tested. A recommendation for future research is that the links between peat structure, peat chemistry and responses to abiotic triggers are thoroughly investigated. The high number of strong multivariate 'best fit' models for individual microforms (15 funnel-trap models had a \( r^2 \) of 0.60 – 0.93) is an indication that temporal variation in ebullition could be reliably predicted using readily-available meteorological data if subsurface controls on bubble formation and accumulation can be established for the most common peat types.
Chapter 7  CONCLUSIONS AND FUTURE RESEARCH

This chapter provides a brief overview of the results of the six hypothesis tests, evaluates the success of the research with respect to the overall project aims and objectives and suggests areas where future research might be directed in order to advance the findings at Cors Fochno, particularly with respect to improving our understanding of the role of ebullition as a transport mechanism of CH$_4$ from peatlands to the atmosphere.

7.1  OVERVIEW OF HYPOTHESIS TEST RESULTS

Of the six original hypotheses four were rejected (HYPOTHESES 1, 2, 4 & 5), although 5 needs further testing, and two partially accepted (partial acceptance of HYPOTHESIS 6 was tentative). Briefly, the results of each hypothesis test were as follows:

HYPOTHESIS 1 – AT AN ANNUAL SCALE, CH$_4$ EMISSIONS VARY SIGNIFICANTLY BETWEEN MICROFORM-TYPES.

There were no significant differences in annually-averaged/totalled CH$_4$ emissions between the microform-types despite distinct differences in water table position between the hummocks and the lawn/hollow microform-type groups. Similar emissions from the different microform-types were explained, in part, by the presence of Rhynchospora alba (a CH$_4$ transporting sedge-species) in all but one of the 20 microforms and the small variation of average water table position between lawns and hollows.

HYPOTHESIS 2 – DIFFERENCES IN PLANT COVER, WATER TABLE POSITION AND NEAR-SURFACE PEAT TEMPERATURE EXPLAIN THE SPATIAL VARIABILITY OF CH$_4$ EMISSIONS BETWEEN MICROFORM-TYPES.

Given the outcome of HYPOTHESIS 1, HYPOTHESIS 2 was rejected with respect to microform-types. However, differences in plant cover and average water table position explained most of the spatial variation of CH$_4$ emissions between individual microforms. Near-surface peat temperature at 20 cm depth was not a significant explanatory factor due to similarities in annually-averaged peat
temperature across the 20 microforms. Average water table position was the most important individual predictor of variation (explaining a third of the spatial variation overall), but the abundance of two key species, Rhynchospora alba and Sphagnum moss, was most relevant for describing spatial variation of both annually-averaged and annually-totalled CH$_4$ emissions. The abundance of Rhynchospora alba was a strong predictor of emissions from mud-bottomed hollows and hummocks. Within the lawn microform-types, there was little variation in the abundance of R. alba and the sedge was not a significant predictor of emissions.

**Hypothesis 3 – Air temperature, solar radiation, rainfall, wind speed, wind direction and barometric pressure are significant controls on temporal variability of CH$_4$ fluxes from each microform-type.**

The response of CH$_4$ fluxes to changes in air temperature, solar radiation, rainfall, wind duration and barometric pressure during the year varied between the different microform-types and the hypothesis could not be accepted in full. **Hypothesis 3** was accepted for the sedge lawns with respect to all abiotic factors except wind speed. For the Sphagnum lawns, the hypothesis was accepted with respect to air temperature, solar radiation and barometric pressure, for the mud-bottomed hollows with respect to air temperature and barometric pressure only and for the hummocks, with respect to air temperature and rainfall only. Air temperature was the most important abiotic control on CH$_4$ fluxes from all microform-types, but explained only 8% of temporal variation from hummocks (the lowest-emitting microform-type). Air temperature was the best predictor for sedge lawns (the highest-emitting microform-type), explaining 37% of temporal variation in CH$_4$ fluxes. The strength of the best fit models for each microform-type ranged from weak to moderate, with $r^2$ values ranging from 0.12 (hummock partial model) to 0.51 (sedge partial model).

**Hypothesis 4 – CH$_4$ ebullition to the water table of mud-bottomed hollows is greater than to the water table of Sphagnum lawns.**

Despite distinct visual differences in peat structure and sedge-root density between the two microform-types, unexpectedly, there was no significant difference between microform-types with respect to seasonal CH$_4$ ebullition to
the water table and HYPOTHESIS 4 was rejected. Throughout the season there was high spatial variability of CH\textsubscript{4} ebullition within both microform-type groups. The controls on this variation require further investigation.

HYPOTHESIS 5 – FOR MOST OF THE SUMMER/EARLY AUTUMN SEASON, CH\textsubscript{4} ARRIVING AT THE WATER TABLE VIA EBULLITION IS OXIDIZED BEFORE REACHING THE ATMOSPHERE.

Based on potential rates of oxidation in near-surface peat during the summer/early-autumn season, it was concluded that most of the time CH\textsubscript{4} arriving at the water table via ebullition would not have been entirely oxidized to CO\textsubscript{2} before reaching the atmosphere. In 11 of the 16 weeks (i.e. for 69\% of the time) CH\textsubscript{4} ebullition to the water table was sufficient to overwhelm rates of methanotrophic processing and substantive ebullition losses of CH\textsubscript{4} occurred. Direct comparison with CH\textsubscript{4} emissions the previous year indicated that ebullition was an important mechanism of CH\textsubscript{4} loss from Cors Fochno to the atmosphere, particularly during late summer and early autumn weeks.

HYPOTHESIS 6 – AIR TEMPERATURE, RAINFALL, WIND SPEED AND CHANGE IN BAROMETRIC PRESSURE ARE IMPORTANT CONTROLS ON EBULLITION. OF THESE, CHANGE IN BAROMETRIC PRESSURE IS THE MOST IMPORTANT.

Due to a spatially-varied response of ebullition to the abiotic variables and different responses at the seasonal and pressure event timescales, HYPOTHESIS 6 could not be fully accepted. Based on analysis of the full seasonal dataset, HYPOTHESIS 6 was accepted with respect to change in barometric pressure, wind speed and air temperature, but not rainfall. At the scale of individual microforms, HYPOTHESIS 6 was accepted fully for one microform, rejected fully for five and partially accepted for 22. Ebullition in most of the microforms (18 out of 28) showed a moderate to strong response to changes in air temperature during the season. Ebullition in six microforms showed a moderate to strong response to variations in barometric pressure and in two microforms a moderate to strong response to rainfall. Ebullition in four microforms showed a weak to moderate response to changes in weekly-averaged wind speed.

The most important abiotic factor controlling temporal variation of ebullition during the two low pressure events was air temperature. Change in barometric
pressure was not a significant control on ebullition to the funnel-traps and there was no evidence of widespread ebullition in response to falling pressure during either event. However, some of the CH₄ flux variation captured using flux-chambers during the second pressure event (where wind speeds were highly variable) may have been due to ebullition in response to short-lived pressure changes.

7.2 SUCCESS OF RESEARCH IN ACHIEVING AIMS & OBJECTIVES

7.2.1 MEASURING MICROFORM-SCALE EMISSIONS VARIATION ACROSS A PATTERNED PEATLAND

The work presented in CHAPTER 4 reflects a successful year of regular CH₄ flux measurements at Cors Fochno and the development of an inexpensive, flexible method for ‘offline’ analysis of headspace gas samples using laser spectroscopy. The success of the latter is reflected in publication of the new MCDA approach for CH₄ analysis in the journal Ecohydrology (Baird et al., 2010a). The robust flux-chamber method produced reliable evidence of CH₄ flux variation throughout the year and between microforms. High spatial variability of emissions was demonstrated clearly as was the importance of wintertime emissions to the CH₄ budget of Cors Fochno. Both findings underlie the importance of spatial replication of flux measurements in future peatland CH₄ flux studies and for fluxes measured outside of spring and summer months.

Given that it was not possible to distinguish emissions via the different flux pathways, the success of the flux-chamber method and sampling regime with respect to the capture of ebullition is hard to evaluate. A ‘best practice’ approach was applied at Cors Fochno with respect to capturing ebullition fluxes using the static flux-chamber method – the most widely applied approach to measuring CH₄ emissions from peatlands. No flux-chamber measurements were rejected on the grounds of non-linearity (as is the case in most flux-chamber studies on peatlands) and the utmost care was taken to minimise observer effect on bubble fluxes before, during and after sampling. There was evidence of episodic release of individual bubbles during chamber operation which demonstrated some success in capturing ebullition. However, the greatest success in capturing ebullition was via the funnel-traps.
CHAPTER 5 presented the results of a successful 16-week investigation of CH$_4$ ebullition variation between 28 microforms. This aspect of the research was completely novel, providing the first evidence of the spatial and temporal variation of ebullition across a patterned peatland during a full summer season. Although HYPOTHESIS 4 was rejected with respect to differences in ebullition between microform types, the hypothesis test result was an important finding, suggesting the importance of localised processes and peat structures as controls on ebullition. The funnel-trap method was a success and demonstrated the relative ease with which a continual record of bubble flux data can be obtained from peatlands. The method used at Cors Fochno had several limitations, notably the monthly sampling of funnel-gas for analysis of CH$_4$ concentration and potential for ‘hotspots’ of ebullition to have been missed due to the small ‘footprint’ of the funnel-traps. The former can be easily addressed in future studies. The latter is a limitation inherent in any method which attempts to quantify a highly variable flux using a ‘bottom-up’ approach and does not negate the success of the study per se. However, there is a need to develop ‘top-down’ approaches for identifying ‘hot’ and ‘cold’ spots of ebullition so that future studies using funnel-traps are effective and provide a reliable picture of spatial variations of ebullition (discussed further in Section 7.3.3).

CHAPTER 5 also reported estimated ebullition losses of CH$_4$ to the atmosphere after accounting for potential methanotrophy above the water table. The main objective of this part of the research was to provide a ‘best estimate’ of CH$_4$ losses to the atmosphere and improve on previous studies using funnel-traps which had assumed all CH$_4$ arriving via ebullition to the water table (or a depth in the peat profile) reached the atmosphere (e.g. Strack et al., 2005; Strack & Waddington, 2008). The main objective was achieved. However, as noted in section 7.1, use of oxidation data from a nearby peatland introduced uncertainty into the test of HYPOTHESIS 5 and subsequent evaluation of the relative importance of ebullition as a mechanism of CH$_4$ transport from Cors Fochno. Further research on the importance of methanotrophic processing with respect to bubble fluxes is needed (discussed further in Section 7.3.2).
7.2.3 Evaluating the importance of the abiotic controls on ebullition

Chapter 6 evaluated the importance of abiotic factors on temporal variation of ebullition, with particular focus on falling barometric pressure – the most widely discussed ‘trigger’ for episodic ebullition. The work reported some interesting findings, particularly with respect to the spatially-varied response of ebullition to changing abiotic conditions during the season and the control of diurnal temperature fluctuations on rates of ebullition. With respect to the importance of falling pressure as an important control on episodic ebullition, no firm conclusions could be drawn from the seasonal data. Due to the high frequency of low pressure systems during the season and the weekly measurement regime, it was difficult to evaluate the importance of falling pressure per se and in this respect, one of the key aims of the seasonal study was not entirely successful. The high-frequency measurement campaigns during the two pressure events were more successful, providing ebullition flux data that could be related directly to individual periods of falling and rising pressure. In both events, falling pressure did not emerge as a significant control on ebullition fluxes to the water table. In conjunction with the seasonal data, this was an important finding, particularly when compared with other research that has investigated the relationship between falling pressure and ebullition in the field (e.g. Tokida et al., 2007). Given the high spatial variability of ebullition, the work presented in Chapter 6 provided the strongest indication to date that falling pressure does not have a uniform effect on ebullition rates across all peatlands and its importance as a ‘trigger’ for episodic ebullition may be dependent on a range of subsurface factors.

7.3 Looking forward

7.3.1 Improvements to future flux-chamber studies at UK peatlands

For reliable estimates of annual CH$_4$ emissions to be derived based on a ‘bottom-up’ approach, there needs to be a universal adoption of ‘best practice’ flux-chamber protocols which (i) increase the probability of capturing ebullition fluxes (i.e. by sampling during a range of weather and pressure conditions), (ii) minimise risk of artificial bubble fluxes during flux-chamber operation, (iii) ensure that ebullition fluxes are retained in the datasets used for peatland emissions estimates and statistical analyses and (iv) ensure that ‘hot’ and ‘cold’ emissions areas are accounted for in the sampling design. While static flux-chambers are not the
optimum method for capturing temporally variable bubble fluxes, they are most widely-used method for measuring CH$_4$ exchange between the peatland and atmosphere. Thus, where they are used such measures should be taken to mitigate underestimates of CH$_4$ emissions.

In the future, effective sampling strategies which account for potential spatial variability in emissions across patterned peatlands (particularly ‘hot’ and ‘cold’ areas of emissions) are particularly important. Due to the scale of potential variability and the logistical and financial constraints on field-based studies, the 'optimum' number of sampling points based on a statistical approach (e.g. Moore et al., 1994) is seldom possible. On the strength of the findings reported in this study, it may be possible to optimise sampling based on observations of small-scale variations in the abundance of key plant species and without the need to sample over a wide area of the peatland. To this end, kite-based aerial photography could be used specifically to map small-scale variations in vegetation cover and identify representative sites for flux-chamber measurements. Detailed information on (often subtle) variations in vegetation cover from kite-based photography would also allow for more reliable scaled-up estimates of CH$_4$ emissions from UK peatlands, particularly where peatland restoration efforts may alter the abundance of CH$_4$-transporting plant species. For areas of a peatland that have been recently restored and are actively regenerating, it would be interesting to conduct a study that combined flux-chamber measurements of CH$_4$ flux with repeated kite-flights over several years in order to monitor changes in the abundance of key plant species and estimate the effect of this change on annual emissions estimates.

It would be useful also to establish a network of peatlands in the UK where automated dynamic chambers were in regular use, allowing for temporal variations in CH$_4$ flux to be examined at a range of timescales. Laser spectroscopy devices (such as the MCDA used in this research) are still expensive and used regularly at a small number of established research sites. Increasing use of such technologies in trace-gas exchange studies will, hopefully, lead to more competitively priced products coming onto the market, making spectroscopy devices more cost-effective and desirable for use in peatland carbon exchange research. Automated dynamic chambers could be used to measure winter emissions, without the logistical difficulties associated with wintertime measurements at often remote
peatland locations. Wintertime emissions are probably important components of the annual CH$_4$ budget from UK peatlands and need to be measured more widely than at present.

### 7.3.2 Evaluating the Importance of Methanotrophy on CH$_4$ Ebullition

Future work is needed to understand the importance of methanotrophy as a control on CH$_4$ ebullition from peat to the atmosphere. Oxidation may reduce the CH$_4$ concentration of bubbles that rise slowly through zones of methanotrophic processing and/or become trapped within pore spaces in the near-surface peat. Peat structure and the size and location of populations of methanotrophs may be important controls on this process and it is possible that the CH$_4$ in transit to the atmosphere is depleted more readily in some peat types than others. However, to date there is no clear evidence for the importance of oxidation as a control on CH$_4$ losses via ebullition.

In future studies it might be possible to use differences in the isotopic signature of bubble-CH$_4$ carbon captured at the water table and above the peat surface to evaluate the importance of oxidation between the water table and atmosphere. Methanotrophic bacteria discriminate against the heavier $^{13}$C isotope, thus, if bubble-CH$_4$ has been partially oxidised (due to bubbles moving slowly or become trapped between the water table (as hypothesised here)), the emitted bubble-CH$_4$ may be enriched in $^{13}$C (Chaser et al., 2000). Chanton (2005) hypothesised that ebullition does not have an isotope fractionation effect on $\delta^{13}$C of CH$_4$ (Chanton, 2005) based on (i) work that demonstrated that the $\delta^{13}$C value of CH$_4$ of released bubbles was no different to that of bubble gas held within the wetland sediment (Chanton et al., 1989) and (ii) an assumption that due to the speed and nature of the ebullition flux, CH$_4$ released via ebullition bypasses the fractionating effect of the water column and/or plant rhizomes (Chanton et al., 1989). This hypothesis needs to be fully tested, particularly for (i) different types of bubble flux – ranging from the slow, steady flux of small (microscopic) bubbles to rapid, large episodic releases, and (ii) different types of peat structure – from open, pore structures of loosely-packed Sphagnum to highly-humified mud-bottomed hollow peat.
7.3.3 INVESTIGATING THE LINK BETWEEN SPATIAL CONTROLS AND TEMPORAL VARIATIONS OF EBUILLITION IN SITU

The spatially-varied response of ebullition at Cors Fochno to changing meteorological conditions indicated the need to (i) investigate the controls of subsurface gas production rates and peat structure on the ebullition response to changes in pressure and temperature and (ii) conduct more well-replicated studies on the controls on ebullition. The research at Cors Fochno suggests that studies which investigate controls on temporal variation of ebullition in the laboratory using two or three peat cores (e.g. Kellner et al., 2006; Ström et al., 2005) or based on discontinuous measurement over short timescales (e.g. Tokida et al., 2005b) have the potential to misrepresent the importance of abiotic factors as drivers of ebullition. There is a clear need for more in situ investigations of the controls on ebullition so to account for CH$_4$ ebullition fluxes which originate at a range of peat depths (i.e. not just in the near-surface) and from peat types with a range of peat structures and types/densities of vascular vegetation. At Cors Fochno it would be interesting to conduct a full growing-season study which combined simultaneous measurements of gas volume below the peat surface (e.g. using ground penetrating radar, see Strack & Waddington, 2008) with measurements of ebullition at the water table using funnel-traps. In the first instance, the study could focus on repeated measurements in 'hot' and 'cold' microforms (with respect to ebullition) identified during this PhD research.

In the future, the 'top-down' approach in development by Dr Ed Hornibrook (University of Bristol) which uses multi-spectral infrared imagery to identify hotspots of CH$_4$ emissions (via ebullition and plant-transport) could be used to identify sites for further investigation. Funnel-trap measurements could be combined with this top-down approach to quantify ebullition from the 'hotspots' and provide valuable information on whether the hotspots of ebullition are generally 'hot' or periodically 'hot' and 'cold'. As demonstrated at Cors Fochno, temporal variations in ebullition can be large and it is possible that sites which are very productive at certain points in time (possibly coincident with the images being taken) may be generally dormant or 'cold'. One of the main benefits of the funnel-trap method is that it provides a continual record of the temporal changes in ebullition and can be deployed widely across a peatland surface with minimal expense. The main limitation is the labour involved in monitoring gas volumes at a high enough temporal resolution such that changes in ebullition in response to
abiotic factors are detected. A NERC-funded project led by Dr Yit Teh (University of St Andrews) is currently underway at Lake Vernwy blanket bog (Powys, Wales) which uses funnel-traps (similar to those used at Cors Fochno) and automated digital cameras which take frequent measurements of entrapped bubble gas volume. If successful, this approach to quantifying temporal variations of ebullition (and the controls thereon) could be used widely in peatland CH₄ research.
Acknowledgements

Firstly, and most importantly, many thanks to my supervisors Andy Baird and Kate Heppell for your enthusiasm, support, encouragement and wisdom during the PhD process.

I am very grateful to Mike Bailey of the Countryside Council for Wales for granting permission to use Cors Fochno and for all his support during the project. Mike, thank you for everything (particularly the 7.30am carpark fry-up on that cold and wet October morning...).

Thanks to Simon Dobinson for co-ordinating field and laboratory supplies throughout the study; to Laura Shotbolt and Sophie Green for all their help and practical support in the laboratory and to Ruth Boogert for allowing me to use the data from her fantastic kite-images of Cors Fochno.

To my office buddies Paul Morris and Steve Forden, thanks for making my first year so much fun.

Finally, huge thanks to Tim, my husband, for his patience and unrelenting support during these past four years. Tim, I couldn’t have done it without you.

The project was funded principally by a Queen Mary, University of London studentship, but was supported also by Andy Baird (who provided funds for the purchase of laboratory equipment and travel via a separate research account) and a University of London Central Research Fund (grant code: CRFT1H5R).
References


mobile photoacoustic method versus a well-established gas chromatographic one. Environmental Science and Technology, 40, 6425-6431, doi:10.1021/es060843b

Los Gatos Research Inc. User Manual for LGR DLT-100 Methane/Carbon Dioxide Analyser. Rev. 08-A, CA, USA.


