4 **Investigation of the effect of environmental controls**

Efforts to reconcile the CH$_3$X budgets have generally focussed on quantifying the terrestrial source and sink terms of CH$_3$Br and CH$_3$Cl, yet knowledge of the mechanisms driving CH$_3$X fluxes and the controls on these fluxes remains limited. Within an ecosystem, the sources and sinks of CH$_3$X can generally be ascribed to vegetation and soils respectively. However, biological systems are inherently complicated and net flux of CH$_3$X to and from the atmosphere depends on the relative rates of CH$_3$X emission and uptake. These are in turn dependant on the soil type and the vegetation type within a particular ecosystem. Additionally, the biological activity in vegetation and soil systems is uniquely affected by external environmental conditions such as air temperature, soil temperature, light intensities and water conditions.

Beyond general trends in CH$_3$X fluxes that coincide with seasonal and diurnal patterns in temperature and light intensity, previous studies have not identified any consistent correlations between environmental parameters and CH$_3$X fluxes. It is intrinsically difficult to identify correlations, if any exist, from in situ field data as the environmental parameters are confounded with each other, for example air temperature and light, and with other factors such as differences between individual sampling points and sampling date. To better control the environmental conditions and tease out any individual correlations, laboratory-based studies have investigated the effect of temperature, light levels and water conditions on CH$_3$X fluxes from model systems including mangroves (Manley, *et al.*, 2007), rice paddies (Redeker and Cicerone, 2004) and Arctic tundra soil cores (Teh, *et al.*, 2009).

CH$_3$X fluxes from wetlands have previously been linked to light intensity, temperature and soil water content, but no consistent trends have emerged. In temperate Irish peatlands, observed diurnal variation in CH$_3$X fluxes correlated strongly with the daily solar radiation cycle (Dimmer, *et al.*, 2001) rather than the air temperature, which only varied by 3–4°C during the 24 h measurement period. Similar findings were reported for temperate Scottish saltmarshes (Drewer, *et al.*, 2004).
2006) where CH$_3$Br emissions observed during a 24 h period, in which there was little variation in air temperature, followed a modelled solar radiation cycle. However, neither of these studies directly correlated in situ solar radiation measurements with CH$_3$X fluxes measured at the same time.

The investigations of CH$_3$X fluxes from two temperate New Hampshire peatlands (White, et al., 2005) found that CH$_3$Br fluxes correlated differently to hydrological conditions and temperature at each site. At the first site there was good correlation between CH$_3$Br fluxes and water level, peat temperature and air temperature, although the degree of correlation differed between the growing seasons, particularly for water level. The CH$_3$Br emissions were greater when the air and peat temperatures were warmer and the water level was lower. In contrast, greater CH$_3$Br emissions were observed from the second New Hampshire peat bog when the water level was higher. The correlation between water level and CH$_3$Br fluxes suggested an aerobic, temperature dependent mechanism for CH$_3$Br fluxes from the first peat bog, but that CH$_3$Br emissions were dependant on water saturated peat at the second peat bog. It should also be noted that the vegetation at the two New Hampshire peat bogs was different and likely to be contributing to variation in CH$_3$Br fluxes.

Soil water content and air temperature were also found to affect CH$_3$Br fluxes from rice plants in field studies and controlled laboratory studies, but the effects of these parameters were secondary to the growth stage of the rice plant and the individual rice cultivar (Redeker and Cicerone, 2004). The general trend was for increased CH$_3$Br emissions at warmer temperatures and increased soil water content. CH$_3$Cl emissions were unaffected by changing water and temperature conditions. Thus the production mechanism for CH$_3$Cl emissions from rice paddy agriculture is thought to be different from that of CH$_3$Br (Redeker and Cicerone, 2004), possibly occurring in the soil before transport to the atmosphere via the rice plant. This study used a shading material to alter the light levels and a temperature-controlled sampling chamber to alter the air temperature.

Further correlation between soil water content and CH$_3$X flux was observed in Alaskan Arctic tundra systems (Teh, et al., 2009). The results from field measurements and laboratory based studies found that greater CH$_3$X uptake occurred
in drier soils and that this was probably due to reduced mechanical transfer of CH$_3$X to the soil rather than reduced microbial activity within the soil.

The inconsistency of the findings between studies suggests that the site, particularly the vegetation within the site, strongly influences CH$_3$X fluxes and that any regulation by external environmental parameters is likely to be specific to a system.

The findings discussed in Chapter 3 identified wetland plants as a source for CH$_3$X, which can be larger or smaller depending on the type of vegetation. Certain wetland soils were found to take up CH$_3$X, but the overall sink strength was small. At the wetland sites investigated in this study, plant-based CH$_3$X emission was subject to seasonal variation controlled by the annual plant growth cycles. However, at many of the sampling points at the four Scottish wetland sites, intra-seasonal variation in CH$_3$X fluxes was also observed. The CH$_3$X fluxes from the four Scottish wetland sites were compared with the recorded external environmental parameters (PAR, total solar radiation, air temperature, soil temperature and water level) to determine if intra-seasonal variation could be explained by changes in these parameters. In addition, the CH$_3$X fluxes from RMB and SMM soil cores, and from $P. australis$ plants grown in sand, were investigated in controlled laboratory conditions to examine the effects of temperature, ‘soil’ water content and PAR intensity.
4.1 Presentation of this chapter and summary of the major findings

This chapter compares the CH₃X fluxes at all of the sampling points at the four wetland sites with the external environmental parameters (light intensity, soil temperature, air temperature and soil water level) measured at the time of sampling. The four sampling sites are discussed individually in Section 4.2. The results from each sampling site are summarized at the end of the relevant sub-section. The results from the environmental manipulation experiments are presented in Sections 4.3-4.5 and the major findings from this chapter are summarized in Section 4.6.

In comparing the seasonal trends in CH₃X fluxes to PAR intensity, air temperature and soil temperature it was found that these parameters acted as drivers for the onset and decline of CH₃Br and CH₃Cl emissions respectively. At ACM4, OCF1-4 and RMB1-4 it was clear that PAR and/or air temperature was the main driver for CH₃Br and/or CH₃Cl emissions from these sampling points. As these two parameters are closely linked and are both likely to be important for initiating and stopping plant growth, it is difficult to attribute the degree to which either parameter is acting as a driver. At the SMM sampling points it was apparent that soil temperature was the driver for increasing CH₃Br emissions at the start of the growing season. This was due to the nature of the *P. australis*, which grow annually from rhizomes below the soil surface. The observation of seasonal trends in CH₃X fluxes that are constrained by external environmental parameters supports a plant based emission process/s. CH₃X uptake at the wetland sampling points, although seasonally dependant at some sites did not appear to be driven by any external environmental parameters.

From the comparison of external environmental parameters and CH₃X fluxes from field data, and controlled experiments with greenhouse grown *P. australis* and soil cores where the environmental conditions were individually manipulated, it was demonstrated that CH₃X fluxes were not directly affected by air temperature, soil moisture or light intensity. The controlled experiments did, however, demonstrate the variability of fluxes within an ecosystem.
The observation of seasonal trends driven by external environmental parameters has implications for future trends in CH$_3$X fluxes if the length of the growing season is altered in a future, changed climate.
4.2 CH$_3$X fluxes from Scottish wetland sites in relation to measured environmental parameters

At each sampling event, the air temperature, enclosure temperature, ground temperature and soil water level were recorded. The total solar radiation and PAR intensities were recorded on site on the day of sampling. The seasonal trends in PAR, air temperature and soil temperature are compared with CH$_3$X fluxes from ACM, OCF, RMB and SMM. For each sampling point within the four wetland sites the total dataset of CH$_3$Br and CH$_3$Cl fluxes was individually compared with the air temperature, enclosure temperature, soil water level, total solar radiation and PAR. The correlation coefficient, $r$, was calculated using Microsoft Excel and then checked for significance using Equation 4.1.

Equation 4.1:

$$t = \frac{|r| \sqrt{n - 2}}{\sqrt{1 - r^2}}$$

The long-term seasonal trends in CH$_3$X fluxes were compared with the long-term seasonal trends in PAR, air temperature, soil temperature and soil water level. It was unnecessary to compare the long-term trends with total solar radiation as total solar radiation intensity is directly proportional to PAR intensity.

4.2.1 CH$_3$X fluxes and environmental parameters at Auchencorth Moss

CH$_3$Br and CH$_3$Cl fluxes from the ACM sampling points were measured from June 2007–June 2009 and from January 2008–June 2009 respectively. The fluxes were compared to the environmental parameters measured at the time of sampling.

4.2.1.1 Average environmental conditions at Auchencorth Moss

The average temperatures and light intensities for all the measured environmental parameters were similar at ACM1–4, Table 4.1.
Table 4.1: Average measured environmental parameters recorded at ACM1-4 between June 2007 and June 2009. The range of values is shown in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Ground temp / °C</th>
<th>Peat water level / cm</th>
<th>Total solar radiation / kW m²</th>
<th>PAR / µmol m² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACM 1</td>
<td>13 (2–23)</td>
<td>18 (3–34)</td>
<td>9 (3–14)</td>
<td>-11 (-29– -6)</td>
<td>0.260 (0.056–0.800)</td>
<td>500 (90–1480)</td>
</tr>
<tr>
<td>ACM 2</td>
<td>12 (1–23)</td>
<td>18 (2–36)</td>
<td>9 (3–14)</td>
<td>-9 (-30– -2)</td>
<td>0.230 (0.020–0.660)</td>
<td>480 (40–1340)</td>
</tr>
<tr>
<td>ACM 3</td>
<td>12 (1–23)</td>
<td>16 (2–30)</td>
<td>9 (3–14)</td>
<td>-12 (-33– -2)</td>
<td>0.220 (0.010–0.610)</td>
<td>430 (20–140)</td>
</tr>
<tr>
<td>ACM 4</td>
<td>12 (1–22)</td>
<td>12 (1–22)</td>
<td>8 (2–4)</td>
<td>-17 (-38– -7)</td>
<td>0.220 (0.000–0.630)</td>
<td>430 (0–1260)</td>
</tr>
</tbody>
</table>

The air temperature, soil temperature, PAR and total solar radiation followed expected seasonal trends at ACM with warmer temperatures and higher PAR/total solar radiation recorded in the summer months compared with the winter months. However, the PAR and total solar radiation were more variable during the summer months compared with the air and soil temperature. The water levels at all sampling points were lower in summer compared with winter.

Unlike temperature (air, ground and enclosure) and light intensity, the peat water level was variable between the four sampling points. ACM3 and ACM4 were located in the higher part of the peat bog where it was presumed the peat water level would be lower. However, while the average peat water level at ACM4 was lower than the average peat water level at ACM1 and ACM2, which were in the lower part of the peat bog, the average peat water level at ACM3 was very similar to ACM1 and ACM2.
4.2.1.2 CH$_3$X fluxes from Auchencorth Moss in relation to selected environmental parameters

The CH$_3$X fluxes from ACM1–4 are shown with the average PAR, air temperature and soil temperature for each sampling event during the total measurement period, June 2007–June 2009, Figure 4.1. The average PAR, air temperature and soil temperature from the sampling events at ACM1–4 are shown as there was typically very little variation in these parameters during sampling events on a particular day.

Figure 4.1: CH$_3$Br compared with PAR (a), air temperature (b) and soil temperature (c). CH$_3$Cl fluxes compared with PAR (d), air temperature (e) and soil temperature (f). For all graphs symbols represent ACM1 (- - -), ACM2 (- -), ACM3 (- - - -), ACM4 (- - - -) and the environmental parameter (PAR, air temperature, soil temperature) (---×---).
The CH$_3$X fluxes from ACM1–3 were comparatively low throughout the entire sampling period, Figure 4.1 (a–f). CH$_3$Br was generally taken up at these three points between June and November, but the seasonal CH$_3$Cl emission patterns were less consistent across the sampling points. The seasonal trends in CH$_3$Br fluxes at ACM1–3 broadly corresponded to seasonal trends in PAR, air temperature and soil temperature. In 2008 significant CH$_3$Br uptake at ACM1–3 began in mid-June as the peak air temperature and soil temperatures were observed, Figure 4.1 (a) and (b). Notably, this was after the peak PAR intensities were recorded. CH$_3$Br uptake continued until December at all three sampling points, although both air and peat temperature had declined to winter minimum levels by this time.

Seasonal trends in the CH$_3$Cl fluxes from ACM1 and ACM2 correspond more closely with seasonal trends in the air temperature and peat temperature rather than PAR intensity, Figure 4.1 (b), (e), (c) and (f). At ACM1 the greatest CH$_3$Cl uptake event coincided with the warmest air and peat temperatures at the beginning of summer, but the magnitude and direction of the CH$_3$Cl fluxes was variable during the winter, Figure 4.1 (e–f). At ACM2 increasing CH$_3$Cl emissions corresponded with increasing air temperature and peat temperature during the summer and CH$_3$Cl uptake was observed during the colder winter months, Figure 4.1 (e–f). The variable CH$_3$Cl fluxes at ACM3 did not correspond to seasonal trends in the air temperature, peat temperature or PAR intensity, Figure 4.1 (d–f).

The CH$_3$X fluxes from ACM4 did follow a seasonal trend that broadly corresponded with seasonal trends in PAR, air temperature and soil temperature, Figure 4.1 (a–f). The early growing season peak in CH$_3$X emissions corresponded to the onset of increasing PAR intensities at the start of the growing season, but preceded the onset of warming air and peat temperatures; Figure 4.1 (b–c) and (e–f). Towards the end of the growing season the CH$_3$X fluxes corresponded better with the declining PAR intensities than with the air or peat temperature. However, the intra-seasonal variation in CH$_3$X flux did not necessarily correspond with intra-seasonal variation in PAR during the 2007 and 2008 growing season. The variation in CH$_3$Br emissions corresponded well with the intra-seasonal variation in air temperature from early-June 2007 to mid-November 2007, Figure 4.1 (b), but this was not observed in 2008 or 2009 for either CH$_3$Br or CH$_3$Cl emissions.
4.2.1.3 CH$_3$X fluxes in relation to peat water level at ACM

The CH$_3$X flux time series were plotted with the peat water level at the individual sampling points to account for variation in the peat water level between ACM1–4, Figure 4.2.
The seasonal pattern in peat water level was similar at all the ACM sampling points. The water levels remained fairly constant for most of the year, but low water events occurred during mid-summer. This was clearly shown in 2008 and appeared to occur in 2009, Figure 4.2 (a–d). In general the intra-seasonal variation in peat water level did not correspond with the intra-seasonal variation in CH$_3$X fluxes. However, during the 2008 low water level period (mid-May to mid-June), maximum CH$_3$Br uptake rates were observed at ACM1, ACM3 and ACM4, Figure 4.2 (a) and (c–d). In addition there were low CH$_3$Cl emissions from ACM4 during this period. However, in July 2009 there were high CH$_3$X emissions from ACM4 despite the low peat water level. At ACM1 and ACM2 the measurements in July 2009 also suggested that CH$_3$X emissions increased as the peat water level decreased, but it is difficult to draw conclusions from the limited 2009 data set.

Figure 4.2: Comparison of CH$_3$X fluxes with peat water level on the day of sampling for ACM1 (a), ACM2 (b), ACM3 (c) and ACM4 (d). Symbols represent CH$_3$Br fluxes (●●●), CH$_3$Cl fluxes (○○○) and peat water level (××).
4.2.1.4 Correlation between CH$_3$X fluxes and measured environmental parameters at ACM

The $r$ values for the linear correlation between CH$_3$X fluxes and all the measured environmental parameters are presented in Table 4.2 and Table 4.3 for CH$_3$Br and CH$_3$Cl respectively.

**Table 4.2:** $r$ values for correlations between measured environmental parameters and CH$_3$Br fluxes at ACM1-4.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Ground temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACM 1</td>
<td>0.42*</td>
<td>0.60*</td>
<td>0.40</td>
<td>-0.34</td>
<td>0.54</td>
<td>0.58</td>
</tr>
<tr>
<td>ACM 2</td>
<td>-0.16</td>
<td>-0.08</td>
<td>-0.41</td>
<td>-0.20</td>
<td>0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>ACM 3</td>
<td>0.13</td>
<td>0.30</td>
<td>0.13</td>
<td>-0.34</td>
<td>0.35</td>
<td>0.37</td>
</tr>
<tr>
<td>ACM 4</td>
<td>0.50*</td>
<td>0.54*</td>
<td>0.52*</td>
<td>-0.25</td>
<td>0.43*</td>
<td>0.37</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$ level.

**Table 4.3:** $r$ values for correlations between measured environmental parameters and CH$_3$Cl fluxes at ACM1-4.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Ground temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACM 1</td>
<td>-0.22</td>
<td>-0.12</td>
<td>-0.35</td>
<td>0.27</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>ACM 2</td>
<td>-0.37*</td>
<td>-0.57*</td>
<td>-0.39</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>ACM 3</td>
<td>0.06</td>
<td>0.19</td>
<td>0.15</td>
<td>0.09</td>
<td>0.33</td>
<td>0.35</td>
</tr>
<tr>
<td>ACM 4</td>
<td>0.57*</td>
<td>0.58*</td>
<td>0.64*</td>
<td>-0.38</td>
<td>0.51</td>
<td>0.36</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$ level.

The results presented in Table 4.2 show that there were significant linear correlations between air temperature, enclosure temperature, and CH$_3$Br fluxes at ACM1 and ACM4. The significant correlation between air temperature and CH$_3$Br fluxes at ACM1 ($r = 0.42$) is unusual as it is driven by the peak uptake rates observed during winter 2008 when the temperatures were coldest. At ACM4, there was significant linear correlation between CH$_3$Br fluxes and total solar radiation, $r = 0.54$. The linear correlation between CH$_3$Br fluxes and water level were all negative (greater CH$_3$Br
uptake at lower water levels), although not significant. These results support the observations in Figure 4.1 that seasonal trends in CH$_3$Br fluxes at ACM1 and ACM4 follow seasonal temperature trends.

Significant correlation between CH$_3$Cl fluxes and air temperature and enclosure temperature were observed from ACM2 and ACM4, Table 4.3. In addition, CH$_3$Cl fluxes were significantly correlated with the peat temperature at ACM4, $r = 0.64$. At ACM2 the correlation between CH$_3$Cl flux and the temperature parameters was negative indicating that greater rates of uptake occurred at higher temperatures.

4.2.1.5 Summary of CH$_3$X fluxes and environmental parameters at ACM

In general the seasonal trends in CH$_3$X fluxes from the ACM sampling points broadly corresponded with the seasonal trends in air temperature, peat temperature and light intensity. However, the intra-seasonal variation in CH$_3$X fluxes did not correspond well with the intra-seasonal variation in the environmental parameters. For this reason the correlation coefficients between CH$_3$X fluxes and environmental parameters were only sometimes significant and did not necessarily reflect how the CH$_3$X fluxes responded to the environmental parameters.

At ACM1–3 the increasing CH$_3$Br uptake corresponded well with the increasing air and peat temperatures at the start of the growing season suggesting that one or other of these parameters is driving the activation of uptake processes. Increasing CH$_3$Cl uptake at the beginning of the growing season corresponded similarly well with increasing air and peat temperatures at ACM1 and ACM2, although not at ACM3. The observation of temperature dependence indicates that the CH$_3$Br uptake process at ACM1–3, and the CH$_3$Cl uptake process at ACM1–2, is bacterially mediated.

The onset of CH$_3$Br and CH$_3$Cl emissions from ACM4 appeared to corresponded better with PAR intensity than either air temperature or peat temperature. These observations indicate that PAR is a driver for CH$_3$X emissions at ACM4, in line with a plant-based emission process at this sampling point, as was suggested in Chapter 3. However, the correlation coefficients did not reflect these observations.
No significant correlation was observed between CH$_3$X emissions and PAR intensity, but the correlation coefficients were significant between CH$_3$X emissions and air temperature.

There were no significant correlations between peat water level and CH$_3$X fluxes from ACM1–4, but particularly low water levels did correspond with greater uptake and reduced emission on a number of occasions. For example, at ACM1 the greatest CH$_3$Cl uptake was observed in conjunction with the lowest peat water levels recorded at this sampling point. Further, the comparatively low CH$_3$X emissions from ACM4 in June 2008 occurred in conjunction with a particularly low water level event. It is possible that the low emissions were as a result of reduced metabolic activity due to drought stress. However, from the data presented here it is not clear if the peat water level is a driver for CH$_3$X uptake as the lowest water levels are confounded with peak summer air and peat temperatures.

4.2.2 CH$_3$X fluxes and environmental parameters at Old Castles Farm

The CH$_3$Br and CH$_3$Cl fluxes measured at the five OCF sampling points from May 2007–June 2009 and from January 2008–June 2009 respectively were compared to the environmental parameters measured at the time of sampling.

4.2.2.1 Average environmental conditions at Old Castles Farm

The average temperatures, soil water level, and light intensities recorded at the OCF sampling points are shown in Table 4.4.
Table 4.4: Average measured environmental parameters recorded at OCF1-5 from May 2007 to June 2009. The range of values is shown in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Soil temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m²</th>
<th>PAR / µmol m² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCF 1</td>
<td>13 (3–20)</td>
<td>19 (3–32)</td>
<td>10 (5–15)</td>
<td>1 (0–3)</td>
<td>0.300 (0.030–0.610)</td>
<td>600 (73–1260)</td>
</tr>
<tr>
<td>OCF 2</td>
<td>13 (3–20)</td>
<td>20 (1–35)</td>
<td>11 (3–20)</td>
<td>-37 (-42– -24)</td>
<td>0.290 (0.020–0.790)</td>
<td>530 (52–1490)</td>
</tr>
<tr>
<td>OCF 3</td>
<td>14 (2–25)</td>
<td>17 (3–34)</td>
<td>11 (4–15)</td>
<td>2 (-1–11)</td>
<td>0.280 (0.020–0.810)</td>
<td>490 (40–1510)</td>
</tr>
<tr>
<td>OCF 4</td>
<td>14 (2–22)</td>
<td>15 (1–28)</td>
<td>11 (4–17)</td>
<td>3 (0–30)</td>
<td>0.300 (0.020–0.810)</td>
<td>580 (42–1510)</td>
</tr>
<tr>
<td>OCF 5</td>
<td>14 (1–23)</td>
<td>15 (3–29)</td>
<td>11 (5–15)</td>
<td>1 (-22-11)</td>
<td>0.270 (0.020–0.720)</td>
<td>560 (40–1390)</td>
</tr>
</tbody>
</table>

The data presented in Table 4.4 shows that the average and the range of air temperature, soil temperature and enclosure temperature were similar at OCF1–5 over the total measurement period. The average water level was just above the ground surface at OCF1 and OCF3–5 showing that these sampling points were generally inundated with water. However, OCF2 was situated on a raised area within the wetland and consequently the soil water level was consistently much lower. This sampling point was intended as a comparison to OCF1 which enclosed similar vegetation, but had a consistently higher water level. The air temperature, soil temperature, PAR and total solar radiation at OCF followed seasonal trends with warmer temperatures and higher light intensities recorded in the summer months compared with the winter months. The light intensities (PAR and total solar radiation) were, however, more variable during the summer months compared with air and soil temperatures. There were no clear seasonal trends in the water level at any of the OCF sampling points.
4.2.2.2 *CH$_3$X* fluxes from Old Castles Farm in relation to selected environmental parameters

The CH$_3$X fluxes measured at OCF1–5 over the total measurement period are plotted with the average PAR intensity, air temperature and soil temperature at OCF on the day of sampling, Figure 4.3. The average PAR, air temperature and soil temperature from the sampling events at OCF1–5 are shown as there was typically very little variation in these parameters between sampling events on a particular day.

Figure 4.3: CH$_3$Br compared with PAR (a), air temperature (b) and soil temperature (c). CH$_3$Cl fluxes compared with PAR (d), air temperature (e) and soil temperature (f). Symbols are consistent between graphs; OCF1 (- -.), OCF2 (- -.), OCF3 (- -.), OCF4 (- -.), OCF5 (- -.) and environmental parameters (PAR, air temperature, soil temperature) (- -x- -).
In general the peak growing season CH$_3$Br emissions from the OCF sampling points occurred within the range of peak growing season air and soil temperatures, Figure 4.3 (b–c). In contrast, the peak growing season CH$_3$Br emissions occurred after the early growing season peak PAR intensity, Figure 4.3 (a). The CH$_3$Cl fluxes from OCF1–5 were generally low and varied between uptake and emission. However, significant fluxes generally occurred during the period of peak air and soil temperatures. There did not appear to be any relationship between CH$_3$Cl fluxes and PAR intensity.

Although the trends in CH$_3$X fluxes, particularly in CH$_3$Br emissions, followed seasonal patterns in air temperature, soil temperature and PAR, the results presented in Figure 4.3 do not show intra-seasonal variation in CH$_3$X fluxes to be a direct result of the light intensity and air temperature on the day of sampling.

4.2.2.3 CH$_3$X fluxes in relation to soil water level at Old Castles Farm

The water level measured at the time of sampling was plotted with the CH$_3$X flux time series for the individual OCF sampling points, Figure 4.4.
Characterisation of CH$_3$X fluxes from Scottish and high latitude wetlands
Catherine Hardacre PhD 2010
The University of Edinburgh

Chapter 4
Figure 4.4: Comparison of CH₃X fluxes with water level on the day of sampling for OCF1 (a), OCF2 (b), OCF3 (c), OCF4 (d) and OCF5 (e). Symbols represent CH₃Br fluxes (••••), CH₃Cl fluxes (○○○○) and peat water level (×).

The time series presented in Figure 4.4 (a–e) show that the soil water level was generally lower in the summer months compared with the winter months, although at OCF1 and OCF5 the water level showed more variation and less seasonal dependence compared with the other sampling points. It should be noted that water levels above the ground surface were originally recorded as ‘zero’ until January 2008. After this time if the water level was above the ground surface, the depth was measured. At OCF4 and OCF5 the sampling points were often inundated with as much as 30 cm of water, Figure 4.4 (d–e).

4.2.2.4 Correlation between CH₃X fluxes and measured environmental parameters at Old Castles Farm

The $r$ values for the linear correlations between CH₃X and all the measured environmental parameters are presented in Table 4.5 and Table 4.6 for CH₃Br and CH₃Cl respectively.
Table 4.5: Summary of $r$ values for correlations between CH$_3$Br fluxes and measured environmental parameters at OCF.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Ground temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCF 1</td>
<td>0.45*</td>
<td>0.50*</td>
<td>0.47*</td>
<td>0.01</td>
<td>0.38</td>
<td>0.47*</td>
</tr>
<tr>
<td>OCF 2</td>
<td>0.26</td>
<td>0.28</td>
<td>0.72*</td>
<td>-0.56*</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>OCF 3</td>
<td>0.45*</td>
<td>0.38</td>
<td>0.45*</td>
<td>-0.18</td>
<td>-0.08</td>
<td>-0.17</td>
</tr>
<tr>
<td>OCF 4</td>
<td>0.41</td>
<td>0.73*</td>
<td>0.26</td>
<td>-0.06</td>
<td>0.25</td>
<td>0.36</td>
</tr>
<tr>
<td>OCF 5</td>
<td>0.59*</td>
<td>0.59*</td>
<td>0.58*</td>
<td>0.03</td>
<td>0.16</td>
<td>0.27</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$

Table 4.6: Summary of $r$ values for correlations between CH$_3$Cl fluxes and measured environmental parameters at OCF.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Ground temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCF 1</td>
<td>0.26</td>
<td>0.15</td>
<td>0.24</td>
<td>0.25</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>OCF 2</td>
<td>-0.14</td>
<td>-0.17</td>
<td>-0.20</td>
<td>0.36</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>OCF 3</td>
<td>0.24</td>
<td>0.39</td>
<td>0.20</td>
<td>-0.12</td>
<td>-0.13</td>
<td>-0.18</td>
</tr>
<tr>
<td>OCF 4</td>
<td>0.47</td>
<td>0.46</td>
<td>0.34</td>
<td>-0.13</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>OCF 5</td>
<td>0.41*</td>
<td>0.31</td>
<td>0.44</td>
<td>-0.22</td>
<td>-0.11</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$

Significant correlations between the air temperature, enclosure temperature and the soil temperature, and CH$_3$Br fluxes were generally observed at the OCF sampling points. In addition the CH$_3$Br fluxes were positively correlated with PAR intensity at OCF1 ($r = 0.47$) and negatively correlated with soil water level at OCF2 ($r = -0.56$), Table 4.5. The negative correlation between the CH$_3$Br fluxes and soil water level indicates that greater CH$_3$Br emissions occurred when the water level was lower. This may simply be due to the low water levels occurring in conjunction with the warmer air temperatures and more intense PAR during summer. The only significant correlation for CH$_3$Cl flux was observed with air temperature at OCF5.
4.2.2.5 Summary of CH$_3$X fluxes and environmental parameters at OCF

The agreement between seasonal trends in CH$_3$Br emissions and temperature parameters (air and soil) suggests that temperature is a driver for the onset of emissions from the vegetation at OCF. The consistent significant correlation between the temperature parameters and the CH$_3$Br emissions reflects this agreement. However, intra-seasonal variation in temperature did not appear to drive intra-seasonal variation in CH$_3$Br emission.

Substantial CH$_3$Cl fluxes from the OCF sampling points tended to occur during the warmer summer months, but did not appear to be driven very strongly by any of the environmental parameters investigated in this study.

4.2.3 CH$_3$X fluxes and environmental parameters at Red Moss of Balerno

CH$_3$Br and CH$_3$Cl fluxes measured at the RMB sampling points from June 2007–July 2009 and from January 2008–July 2009, respectively, were compared to environmental parameters measured at the time of sampling.

4.2.3.1 Average environmental conditions at Red Moss of Balerno

The average temperatures, light intensities and peat water levels from each RMB sampling point over the total measurement period are shown in Table 4.7. The peat water level was not monitored at RMB5–8. The air temperature, soil temperature, PAR and total solar radiation followed seasonal trends at RMB; warmer temperatures and greater light intensities were recorded in the summer months compared with the winter months. The average air temperature, peat temperature, enclosure temperature, PAR and total solar radiation for the total sampling period were found to be similar at RMB1–4.
Table 4.7: The average measured environmental parameters recorded at RMB1-8 from June 2007 to July 2009. The range of values is shown in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Peat temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m(^{-2})</th>
<th>PAR / µmol m(^{-2}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMB 1</td>
<td>12</td>
<td>16</td>
<td>9</td>
<td>-33</td>
<td>0.260</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td>(0–26)</td>
<td>(4–34)</td>
<td>(1–15)</td>
<td>(-42– -16)</td>
<td>(0.020–0.670)</td>
<td>(40–1320)</td>
</tr>
<tr>
<td>RMB 2</td>
<td>12</td>
<td>16</td>
<td>9</td>
<td>-7</td>
<td>0.270</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td>(1–27)</td>
<td>(3–37)</td>
<td>(1–16)</td>
<td>(-36–0)</td>
<td>(0.020–0.930)</td>
<td>(40–530)</td>
</tr>
<tr>
<td>RMB 3</td>
<td>12</td>
<td>17</td>
<td>9</td>
<td>-18</td>
<td>0.272</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td>(0-27)</td>
<td>(4–40)</td>
<td>(1–18)</td>
<td>(-31– -11)</td>
<td>(0.000–0.700)</td>
<td>(20–1410)</td>
</tr>
<tr>
<td>RMB 4</td>
<td>12</td>
<td>15</td>
<td>9</td>
<td>-2</td>
<td>0.330</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>(2–27)</td>
<td>(4–35)</td>
<td>(1–23)</td>
<td>(-10– -1)</td>
<td>(0.010–0.840)</td>
<td>(0–1600)</td>
</tr>
<tr>
<td>RMB 5</td>
<td>9</td>
<td>13</td>
<td>6</td>
<td>-</td>
<td>0.240</td>
<td>490</td>
</tr>
<tr>
<td></td>
<td>(3-17)</td>
<td>(4–26)</td>
<td>(2–13)</td>
<td></td>
<td>(0.020–0.830)</td>
<td>(40–1600)</td>
</tr>
<tr>
<td>RMB 6</td>
<td>9</td>
<td>14</td>
<td>7</td>
<td>-</td>
<td>0.260</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>(3–18)</td>
<td>(5–27)</td>
<td>(2–14)</td>
<td></td>
<td>(0.020–0.930)</td>
<td>(50–1810)</td>
</tr>
<tr>
<td>RMB 7</td>
<td>9</td>
<td>13</td>
<td>7</td>
<td>-</td>
<td>0.150</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>(3–14)</td>
<td>(5–22)</td>
<td>(2–14)</td>
<td></td>
<td>(0.010–0.370)</td>
<td>(0–780)</td>
</tr>
<tr>
<td>RMB 8</td>
<td>9</td>
<td>13</td>
<td>7</td>
<td>-</td>
<td>0.160</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>(3–17)</td>
<td>(5–22)</td>
<td>(2–14)</td>
<td></td>
<td>(0.010–0.400)</td>
<td>(20–840)</td>
</tr>
</tbody>
</table>

The shorter sampling period at RMB5–8 (September 2008–July 2009) did not include a full summer season and the average air temperature, peat temperature and enclosure temperature was lower at these sampling points, Table 4.7. The average PAR and total solar radiation was also lower at RMB7 and RMB8 compared with RMB1–4. However, at RMB5 and RMB6 the average PAR and total solar radiation was similar to the average light intensities at RMB1–4. This was driven by particularly high values recorded at these two sampling points on 09/07/09.

The peat water levels were variable at RMB1–4, as designed in the experimental set up, Chapter 2. The average peat water level at RMB1 and RMB3, which were situated on hummocks, was lower than the average peat water level at RMB2 and RMB4, which were situated in hollows, Table 4.7. Further, the peat water level was
lower at RMB1, in the raised part of the peat bog, compared with the water level at RMB3 in the lower part of the peat bog.

4.2.3.2  **CH$_3$X fluxes from Red Moss of Balerno in relation to selected environmental parameters**

The average PAR, air temperature and soil temperature recorded on the day of sampling are plotted with the CH$_3$X flux time series from RMB1–4 in Figure 4.5. The average PAR, air temperature and soil temperature are shown as there was typically very little variation in these parameters during sampling events over a particular day. The comparatively short time series for RMB5–8 are not shown here, but the correlations between CH$_3$X fluxes from these sampling points and the measured environmental parameters are presented in Section 4.2.3.4, Table 4.8 and Table 4.9.
Figure 4.5: CH$_3$Br compared with PAR (a), air temperature (b) and soil temperature (c). CH$_2$Cl fluxes compared with PAR (d), air temperature (e) and soil temperature (f). Symbols are consistent for all graphs; RMB1 (-○-), RMB2 (-▲-), RMB (-△-), RMB4 (-○-), and the environmental parameter (PAR, air temperature, soil temperature) (×-×-).

The seasonal trends in CH$_3$X emissions from RMB1, RMB2 and RMB3 corresponded well with the seasonal trends in air temperature and PAR, Figure 4.5 (a–b) and (d–f). The CH$_3$X fluxes from RMB4 were comparatively low and significant fluxes were only observed during the growing season, Figure 4.5 (a–f). The onset of increasing CH$_3$X emissions at the start of the growing season corresponded with the onset of warmer air temperatures, peat temperatures and higher PAR intensities. During mid-winter the cooler air temperatures and lower PAR intensities corresponded with lower CH$_3$X fluxes.
At RMB1, RMB2 and RMB3, peaks in the CH$_3$Br and CH$_3$Cl emissions between early-May 2008 and late-August 2008 corresponded with peaks in air temperature and PAR at this time, Figure 4.5 (a–b) and (d–e). Specifically, the large CH$_3$Br and CH$_3$Cl emission peaks observed at RMB1–3 on 08/05/08 corresponded with the highest PAR intensity and warmest air temperature measured in 2008. However, the warmest peat temperatures were recorded after the early-growing season peak in CH$_3$X emissions, Figure 4.5 (c) and (f).

There was less agreement between the intra-seasonal variation in CH$_3$X emissions and air temperature, peat temperature, and PAR at RMB1–3 during the 2007 (CH$_3$Br only) and 2009 growing seasons. Although peaks in air temperature and PAR were recorded during the 2007 and 2009 growing seasons, there were no corresponding peaks in CH$_3$Br or CH$_3$Cl emissions, Figure 4.5 (a–b), (d–e). Further, CH$_3$Cl emissions did not begin to increase with the onset of warmer air temperatures and higher PAR at the beginning of the 2009 growing season.

The CH$_3$Br uptake from RMB4 was not usually significant, but the greatest uptake did occur between mid- and late-June in conjunction with the warmest air temperatures and highest light intensities. However, these uptake events were before the warmest peat temperatures were recorded. The CH$_3$Cl emissions from RMB4, although much lower than the emissions from RMB1–3, also followed seasonal trends in the air temperature and PAR. The onset of increasing CH$_3$Cl emissions corresponded well with the onset of increasing PAR and air temperature at the start of the growing season, but the CH$_3$Cl emissions began to decline before the PAR and air temperature decreased towards the end of the growing season. As at RMB1–3, the peak CH$_3$Cl emissions from RMB4 were observed before the peak growing season peat temperatures occurred.
4.2.3.3 \( \text{CH}_3X \) fluxes in relation to peat water level at Red Moss of Balerno

The peat water level measured at the time of sampling was plotted with the time series for \( \text{CH}_3\text{Br} \) and \( \text{CH}_3\text{Cl} \) fluxes for each of RMB1–4, Figure 4.6 (a–d).
Intra-site variation in the peat water level was greatest between ‘hummock’ sampling points (RMB1 and RMB3) and ‘hollow’ sampling points (RMB2 and RMB4) rather than between the raised and lower areas of the bog, Section 4.2.3.1 and Table 4.7. At the ‘hollow’ sampling points (RMB2 and RMB4) the peat water level was consistently high during winter, but variable during summer when periods of very low water were recorded. These summertime low-water events corresponded with increased CH$_3$X emissions from RMB2 and significant CH$_3$Br uptake at RMB4 during the 2008 growing season. In contrast, the peat water level was variable throughout the year at the ‘hummock’ sampling points (RMB1 and RMB3), but the intra-seasonal variation in the peat water level did not correspond well with intra-seasonal variation in CH$_3$X fluxes at RMB1 and RMB3.

4.2.3.4 Correlation between CH$_3$X fluxes and measured environmental parameters at Red Moss of Balerno

The correlation coefficients, $r$, for the liner correlation between CH$_3$X fluxes and the measured environmental parameters are presented in Table 4.8 and Table 4.9 for CH$_3$Br and CH$_3$Cl respectively.
Table 4.8: Summary of correlation coefficients for correlations between CH$_3$Br fluxes and measured environmental parameters at RMB.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Peat temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMB 1</td>
<td>0.45*</td>
<td>-0.09</td>
<td>0.11</td>
<td>0.01</td>
<td>0.41</td>
<td>0.38</td>
</tr>
<tr>
<td>RMB 2</td>
<td>0.69*</td>
<td>0.36</td>
<td>0.38</td>
<td>-0.27</td>
<td>0.49*</td>
<td>0.47*</td>
</tr>
<tr>
<td>RMB 3</td>
<td>0.15</td>
<td>0.03</td>
<td>-0.22</td>
<td>0.13</td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td>RMB 4</td>
<td>-0.36</td>
<td>0.35</td>
<td>0.35</td>
<td>0.53*§</td>
<td>-0.20</td>
<td>-0.27</td>
</tr>
<tr>
<td>RMB 5</td>
<td>-0.49*†</td>
<td>-0.41*†</td>
<td>-0.22†</td>
<td>-</td>
<td>-0.26</td>
<td>-0.26</td>
</tr>
<tr>
<td>RMB 6</td>
<td>0.13</td>
<td>0.13</td>
<td>-0.26</td>
<td>-</td>
<td>-0.20</td>
<td>-0.21</td>
</tr>
<tr>
<td>RMB 7</td>
<td>0.69*†</td>
<td>0.64*†</td>
<td>0.45*†</td>
<td>-</td>
<td>0.63*†</td>
<td>0.61*†</td>
</tr>
<tr>
<td>RMB 8</td>
<td>0.04</td>
<td>-0.16</td>
<td>0.17</td>
<td>-</td>
<td>0.06</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$
† <5 data points
§ Significant correlation driven by outliers

Table 4.9: Summary of correlation coefficients for correlations between CH$_3$Cl fluxes and measured environmental parameters at RMB.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Peat temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMB 1</td>
<td>0.75*</td>
<td>0.51*</td>
<td>0.66*</td>
<td>-0.51*</td>
<td>0.66*</td>
<td>0.66*</td>
</tr>
<tr>
<td>RMB 2</td>
<td>0.53*</td>
<td>0.25</td>
<td>0.26</td>
<td>-0.45</td>
<td>0.53*</td>
<td>0.50</td>
</tr>
<tr>
<td>RMB 3</td>
<td>0.76*</td>
<td>0.74*</td>
<td>0.58*</td>
<td>-0.31</td>
<td>0.80*</td>
<td>0.79*</td>
</tr>
<tr>
<td>RMB 4</td>
<td>0.60*</td>
<td>0.40</td>
<td>0.31</td>
<td>-0.53*</td>
<td>0.52*</td>
<td>0.54*</td>
</tr>
<tr>
<td>RMB 5</td>
<td>-0.76*†</td>
<td>-0.70*†</td>
<td>-0.59*</td>
<td>-</td>
<td>-0.81*</td>
<td>0.79*</td>
</tr>
<tr>
<td>RMB 6</td>
<td>0.45*</td>
<td>0.18</td>
<td>0.30</td>
<td>-</td>
<td>0.84*†</td>
<td>0.82*†</td>
</tr>
<tr>
<td>RMB 7</td>
<td>0.79*†</td>
<td>0.87*†</td>
<td>0.73*†</td>
<td>-</td>
<td>0.86*†</td>
<td>0.97*</td>
</tr>
<tr>
<td>RMB 8</td>
<td>-0.44*</td>
<td>-0.42</td>
<td>0.27</td>
<td>-</td>
<td>-0.24</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

* Substantial correlations at $P = 0.05$
† <5 data points

The results presented in Table 4.8 and Table 4.9 show that the CH$_3$Cl emissions from RMB1–3 were better correlated with the measured environmental parameters, particularly air temperature and light intensity, than the CH$_3$Br emissions from these
three sampling points. The CH$_3$Cl emissions were significantly correlated with air temperature and light intensity (PAR and total solar radiation) at RMB1–3 and with peat water level (negative correlation) at RMB1, Table 4.9. The negative correlation between CH$_3$Cl emissions and peat water level at RMB1 ($r = -0.51$) indicates that higher emissions were observed at lower water levels. The CH$_3$Br emissions were significantly correlated with air temperature at RMB1 ($r = 0.45$), RMB2 ($r = 0.69$), and with light intensity at RMB2 ($r_{\text{Total solar radiation}} = 0.49$, $r_{\text{PAR}} = 0.47$), Table 4.8.

At RMB4 the CH$_3$Cl fluxes were significantly correlated with air temperature ($r = 0.60$), light intensity ($r_{\text{Total solar radiation}} = 0.52$, $r_{\text{PAR}} = 0.54$) and significantly negatively correlated with peat water level ($r = -0.53$). CH$_3$Br fluxes at RMB4 were only significantly correlated with peat water level ($r = 0.53$). The positive correlation indicating that greater uptake was observed at lower peat water levels. Although it is important to note that significant CH$_3$Br uptake was only observed from RMB4 at the lowest water levels, the significant correlation between CH$_3$Br uptake and peat water level was driven by just three data points.

At RMB5–8 significant correlations were observed between CH$_3$X fluxes and several of the environmental parameters, e.g. between CH$_3$Cl fluxes and air temperature, Table 4.8 and Table 4.9. However, because the datasets for these sampling points were so limited, with a maximum of eight data points at each sampling point, the relevance of these correlations is questionable. The limited datasets for RMB5–8 also resulted in some negative correlations between the CH$_3$X fluxes and certain environmental parameters.

4.2.3.5 Summary of CH$_3$X fluxes and environmental parameters at RMB

The results from RMB1–3 indicate that greater CH$_3$Br and CH$_3$Cl emissions are more likely to occur on warmer, lighter days, but that these environmental conditions will not necessarily result in greater CH$_3$X emissions, particularly CH$_3$Br emissions. In addition, from the data presented in this study it is apparent that the CH$_3$X fluxes will not necessarily respond to environmental parameters in the same way from one season to the next. Because the average temperature and light intensity parameters were similar between the 2007 and 2008 growing seasons, differences in the seasonal
responses of CH₃X fluxes to these parameters is more likely to arise from the particular climatic conditions of a particular year.

The observation of agreement between PAR intensity, air temperature and CH₃Cl emissions during the growing season was corroborated by significant correlation between CH₃Cl emissions and air temperature and PAR at RMB1, RMB2 and RMB3. The absence of significant correlation between PAR intensity, air temperature and CH₃Br emissions, despite the similarities in the seasonal trends, reflected the observations that 1) peaks in air temperature and PAR were not always associated with a peak in CH₃Br flux and 2) the magnitude of the air temperature or PAR peak did not necessarily correspond to the magnitude of the CH₃Br emission peak, particularly in 2007 and 2009.

Peat temperature appeared to be a less important driver for CH₃X emissions from RMB1–4 than air temperature and PAR intensity. The general seasonal trends in CH₃X emission followed increasing and declining peat temperatures at the beginning and end of the growing season, but the peak CH₃X emissions tended to occur before the peak summer peat temperatures. Intra-seasonal variation in the CH₃X emissions meant that the flux values and peat temperatures, which showed very little intra-seasonal variation, were not significantly correlated.

It is likely that peat water level was driving the CH₃Br uptake events on 08/05/08 and 11/06/08. The peat water level was usually very high at this sampling point and it is possible that the lower water levels allowed for greater transport of CH₃Br from the atmosphere to the peat. At RMB1 and RMB2 the link between increased CH₃Cl fluxes and lower water levels is more tenuous because the low water levels coincided with the warmer and lighter summer conditions.

It was demonstrated in Chapter 3 that the CH₃Br and CH₃Cl emissions from RMB1–3 are most likely of plant origin (Calluna vulgaris) and that the emissions are in some way linked to plant metabolic activity. The correlation between air temperature, PAR intensity and CH₃X emissions indicates the plant production process responds to either air temperature, PAR intensity, or both as the dependence of these two parameters on each other makes it difficult to determine which one affects the CH₃X
emissions. The results presented in Chapter 3 also suggested that there were different processes leading to the emission of CH$_3$Br and CH$_3$Cl. The better correlation between CH$_3$Cl emissions air temperature and PAR compared with CH$_3$Br emissions provides further evidence for this, perhaps indicating that CH$_3$Br emissions are less closely coupled to plant-activity than CH$_3$Cl emissions. Although the origin of the CH$_3$Cl emissions from RMB4 was different from the *C. vulgaris* origin at RMB1–3, the agreement between CH$_3$Cl fluxes, PAR and air temperature at this sampling site suggests that the emission process is also plant-based.

The relatively short time series for CH$_3$X fluxes from RMB5–8 means that it is difficult to relate trends in CH$_3$X fluxes to the environmental parameters. However, it is unlikely that there were genuinely negative correlations between CH$_3$X fluxes and environmental parameters such as air temperature and light intensity.

### 4.2.4 CH$_3$X fluxes and environmental parameters at St Margaret’s Marsh

The CH$_3$Br and CH$_3$Cl fluxes were measured at the SMM sampling points from June 2007–July 2009 and from January 2008–July 2009 respectively, and were compared to the environmental parameters measured at the time of sampling.

**4.2.4.1 Average environmental conditions at St Margaret’s Marsh**

The average temperatures, light intensities and peat water level from each SMM sampling point for the total measurement period are shown in Table 4.10.
Table 4.10: Average measured environmental parameters recorded at SMM1-4 from June 2007 to July 2009. The range of values is shown in brackets.

<table>
<thead>
<tr>
<th>Location</th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Soil temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m⁻²</th>
<th>PAR / µmol m⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMM 1</td>
<td>15 (5–28)</td>
<td>14 (5–21)</td>
<td>10 (2–17)</td>
<td>-2 (-14–0)</td>
<td>0.250 (0.020–0.60)</td>
<td>530 (50–1350)</td>
</tr>
<tr>
<td>SMM 2</td>
<td>14 (4–28)</td>
<td>13 (5–20)</td>
<td>10 (2–15)</td>
<td>-2 (-14–0)</td>
<td>0.250 (0.010–0.880)</td>
<td>530 (40–1660)</td>
</tr>
<tr>
<td>SMM 3</td>
<td>14 (4–28)</td>
<td>14 (5–22)</td>
<td>10 (1–16)</td>
<td>-12 (-35–30)</td>
<td>0.260 (0.010–0.670)</td>
<td>530 (30–1350)</td>
</tr>
<tr>
<td>SMM 4</td>
<td>14 (5–28)</td>
<td>13 (3–21)</td>
<td>10 (1–16)</td>
<td>-13 (-35–30)</td>
<td>0.250 (0.010–0.850)</td>
<td>560 (30–1600)</td>
</tr>
</tbody>
</table>

The air temperature, soil temperature, PAR and total solar radiation followed the expected seasonal trends at SMM with warmer temperatures and higher light intensity in the summer months compared with the winter months, Table 4.10. The average air temperature, soil temperature, enclosure temperature, PAR and total solar radiation were similar between SMM1–4, but the average water level was higher at the wetter sites (SMM1 and SMM2) compared with the drier sites (SMM3 and SMM4).

4.2.4.2 CH₃X fluxes from St Margaret's Marsh in relation to selected environmental parameters

The average PAR intensity, air temperature and soil temperature recorded on the day of sampling are plotted with the CH₃X flux time series from SMM in Figure 4.7. The average PAR, air temperature and soil temperature from the sampling events at SMM1–4 are shown as there was typically very little variation in these parameters between sampling events over a particular day.
Figure 4.7: CH$_3$Br compared with PAR (a), air temperature (b) and soil temperature (c). CH$_3$Cl fluxes compared with PAR (d), air temperature (e) and soil temperature (f). Symbols are consistent for all graphs; SMM1 (-○-), SMM2 (-□-), SMM (-Λ-), SMM4 (-◇-) and the environmental parameter (PAR, air temperature, soil temperature) (-×-).

The well-defined seasonal trend in CH$_3$Br emissions from SMM1–4 broadly corresponded with seasonal trends in the air temperature and PAR (Figure 4.7 (a–b)), which were highest between mid-March and early-November. However, the CH$_3$Br emission period, from late-April to mid-October, corresponded most closely to the period of warmest soil temperatures, Figure 4.7 (c). There was little intra-seasonal variation in the CH$_3$Br emissions from SMM1–4, although lower emissions
corresponded with lower light intensity and air temperature SMM3 and with lower air temperatures at SMM4. The CH$_3$Cl fluxes from the SMM sampling points were more erratic than the CH$_3$Br fluxes and did not follow any seasonal trends or appear to be linked to intra-seasonal variation in air temperature, PAR or soil temperature.

4.2.4.3 CH$_3$X fluxes in relation to soil water level at St Margaret’s Marsh

The water level measured at the time of sampling was plotted with the CH$_3$X flux time series for the individual SMM sampling points, Figure 4.8.
At SMM1 and SMM2 there was more variation in the soil water level during the summer compared with the winter, with more low water events being recorded in summer, Figure 4.8 (a–b). However, the variation in water level did not appear to affect the $\text{CH}_3\text{Br}$ emissions at either of these sampling points. There was no distinct seasonal trend in the water level at SMM3 and SMM4, Figure 4.8 (c–d). The soil water level did affect the $\text{CH}_3\text{Cl}$ fluxes at SMM1; at lower soil water levels there was less emission (more uptake) of $\text{CH}_3\text{Cl}$ and at higher soil water levels there was more $\text{CH}_3\text{Cl}$ emission. $\text{CH}_3\text{Cl}$ flux and water level did not correspond with each other at any of SMM2–4. The high water level event on 15/01/2008 where the water was 30 cm above the ground surface was due to flooding in the western (usually drier) section of the marsh.
4.2.4.4 Correlation between CH$_3$X fluxes and measured environmental parameters at St Margaret’s Marsh

The correlation coefficients, $r$, for the linear correlation between CH$_3$X fluxes and the measured environmental parameters are presented in Table 4.11 and Table 4.12 for CH$_3$Br and CH$_3$Cl respectively.

### Table 4.11 Summary of $r$ values for correlations between CH$_3$Br fluxes and measured environmental parameters at SMM.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Soil temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMM 1</td>
<td>0.39</td>
<td>0.39</td>
<td>0.69*</td>
<td>-0.37</td>
<td>0.13</td>
<td>0.30</td>
</tr>
<tr>
<td>SMM 2</td>
<td>0.59*</td>
<td>0.55*</td>
<td>0.70*</td>
<td>-0.45*</td>
<td>0.36</td>
<td>0.42</td>
</tr>
<tr>
<td>SMM 3</td>
<td>0.47*</td>
<td>0.64*</td>
<td>0.62*</td>
<td>-0.38</td>
<td>0.64*</td>
<td>0.53*</td>
</tr>
<tr>
<td>SMM 4</td>
<td>0.56*</td>
<td>0.49*</td>
<td>0.68*</td>
<td>-0.12</td>
<td>0.30</td>
<td>0.53</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$

### Table 4.12: Summary of $r$ values for correlations between CH$_3$Cl fluxes and measured environmental parameters at SMM.

<table>
<thead>
<tr>
<th></th>
<th>Air temp / °C</th>
<th>Enclosure temp / °C</th>
<th>Soil temp / °C</th>
<th>Water level / cm</th>
<th>Total solar radiation / kW m$^{-2}$</th>
<th>PAR / µmol m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMM 1</td>
<td>0.25</td>
<td>0.09</td>
<td>0.53</td>
<td>0.04</td>
<td>0.27</td>
<td>0.25</td>
</tr>
<tr>
<td>SMM 2</td>
<td>0.18</td>
<td>0.10</td>
<td>0.22</td>
<td>0.01</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>SMM 3</td>
<td>0.44</td>
<td>0.50</td>
<td>0.60*</td>
<td>-0.47*</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>SMM 4</td>
<td>0.09</td>
<td>-0.06</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Significant correlation at $P = 0.05$

CH$_3$Br emissions were significantly correlated with soil temperature at SMM1–4 and with air temperature and enclosure temperature at SMM2–4, Table 4.11. The correlation between CH$_3$Br emissions and light intensity and soil water level were generally not significant. The significant correlation between PAR and CH$_3$Br emission at SMM3 (Table 4.11) was driven by the observations in 2007 where trends in PAR intensity and CH$_3$Br emission did correspond well during the growing season, Figure 4.7 (a). The CH$_3$Cl fluxes from SMM1–4 were highly variable and substantial.
correlations were only observed between CH₃Cl fluxes and soil temperature and water level at SMM3, Table 4.12.

4.2.4.5 *Summary of CH₃X fluxes and environmental parameters at SMM*

The observation of coincident seasonal trends in CH₃Br emissions and soil temperature at SMM1–4 resulted in strong correlation coefficients between 0.6 and 0.7 for these two factors and implicates soil temperature as a driver for CH₃Br emission from *P. australis*. The *P. australis* are annual plants that re-grow each year from rhizomes buried up to 1 m below the soil surface. Being underground, soil temperature rather than air temperature or PAR, is a more likely driver for initiation of spring growth and it can be seen that CH₃Br emissions were only observed after a soil temperature of ~7°C was reached.

Although the CH₃Br emissions were also significantly correlated with the air temperature, the correlation was less strong (*r* = 0.47–0.64) than for soil temperature. This reflects the longer period of ‘elevated’ growing season air temperatures compared with the CH₃Br emission period. The positive correlation most likely arose from the general agreement between the seasonal trend in air temperature and CH₃Br emissions.

The absence of correlation between the CH₃Br emissions and PAR levels at most of the SMM sampling points indicates that this parameter is not an important driver of CH₃Br emission at SMM. These results reflect the observations that PAR intensity increased before CH₃Br emission started at the beginning of the growing season. There was also a lot of intra-seasonal variation in PAR, but very little in the CH₃Br emissions.

Although they were not generally significant, the correlations between CH₃Br emissions and soil water level were negative, indicating that CH₃Br emissions were greater when the water level was lower. This may simply be due to confounding of the various parameters, *i.e.* drier conditions occurring in summer when the CH₃Br emissions were greater anyway. However, drier soil may facilitate increased transport of CH₃Br produced in the rhizomes up to the ground surface.
4.3 Field-based shading experiments

It is difficult to attribute a single environmental parameter as directly influencing CH$_3$X fluxes in field studies because variation in the environmental parameters is inter-related and seasonally dependent. For example, sunny summer days are also likely to be warm and soil water levels are more likely to be lower. In addition, the individual environmental parameters could be affecting the CH$_3$X fluxes to varying degrees. For example, if warmer air temperatures and higher light intensities increase CH$_3$X emissions, how will emissions respond to warmer temperatures on a cloudy day? The inter-dependence of the external environmental parameters means it is difficult to study the effect of a single parameter in the field without complex manipulations of the natural environment. However, light intensity can be relatively easily manipulated by shading the plants with a suitable material.

To investigate the effect of reduced light intensity on the CH$_3$X fluxes at the individual sampling points in situ, shading studies were performed. The aim of these experiments was to determine if light intensity directly affected CH$_3$X flux.

4.3.1 Experimental set up for shading manipulations

The shading experiments were performed at all sampling points at the four Scottish wetland sites between June and July 2009. The sampling collars were firstly enclosed for 10 minutes, as normal, to collect a control sample. The chambers were removed to flush the sampling point and then a second enclosure was performed where the entire chamber was covered with a green shading material that reduced the PAR and total solar radiation incident on the enclosed vegetation by approximately 80%. At RMB2, RMB8, SMM2 and SMM4 a 30 minute shaded enclosure was also performed. The CH$_3$X fluxes in ng m$^{-2}$ h$^{-1}$ measured in the shaded and non-shaded enclosures were compared at each sampling point.
4.3.2 Shading studies at Auchencorth Moss

The shading experiments were performed at the ACM sampling points on 22/06/2009. The CH₃Br and CH₃Cl fluxes for shaded and non-shaded closures are presented in Figure 4.9.

![Figure 4.9: Shading experiments for CH₃Br (a) and CH₃Cl (b) fluxes at ACM1-4. Bars represent the analytical uncertainty in CH₃X flux.](image)

CH₃Br fluxes were significantly different between shaded and non-shaded enclosures at ACM1, ACM2 and ACM4, Figure 4.9 (a). There was no significant difference in CH₃Cl fluxes from shaded and non-shaded enclosures at any of the ACM sampling points, Figure 4.9 (b). On the day of sampling, no significant CH₃X fluxes were observed from ACM3 and no significant CH₃Cl fluxes were observed at ACM1,
before or after the shading experiment, although this is not unexpected as CH$_3$X fluxes from ACM1–3 were low and variable throughout the growing season (Chapter 3).

At ACM1 no significant CH$_3$Br fluxes were observed when the vegetation was shaded and at ACM2 no significant fluxes were observed under the control conditions. However, at ACM2 CH$_3$Br uptake was observed when the vegetation was shaded. Somewhat counter-intuitively, significantly higher CH$_3$Br fluxes were observed from ACM4 when the vegetation was shaded. The difference between the air temperature and the enclosure temperature for the non-shaded and shaded enclosures at ACM1–4 was not greater than 3°C.

The difference in CH$_3$Br fluxes between the shaded and non-shaded enclosures at ACM1, ACM2 and ACM4 was greater than the variation in CH$_3$Br fluxes measured during daylight hours (Chapter 3) at these sampling points. It is possible that drastically decreasing the incident light to the vegetation at ACM1 and ACM2 reduced or prevented CH$_3$Br emissions. In the case of ACM2, this allowed CH$_3$Br uptake to become the dominant flux process. Although the data presented here is very limited, the different responses of CH$_3$Br and CH$_3$Cl fluxes to reduced light intensity may provide further evidence for different flux processes for each gas.

It is unlikely that the increased CH$_3$Br emissions from ACM4 were a direct result of shading the vegetation. Although this increase was greater than the diurnal variation measured on 11/08/2008, it is probable that it is the result of intrinsic variation in the CH$_3$Br fluxes from the sampling point.
4.3.3 Shading studies at Old Castles Farm

The shading experiments were performed at the OCF sampling points on 18/06/2009. The CH$_3$Br fluxes for shaded and non-shaded closures are presented in Figure 4.10. No CH$_3$Cl data was available for the shading study at OCF.

![Figure 4.10: Shading experiments for CH$_3$Br fluxes at OCF1-5. Bars represent the analytical uncertainty in CH$_3$Br flux.](image)

Although there is a significant difference between the CH$_3$Br emissions from OCF1 and OCF2, it is very close to not being significant. The overall conclusion for all OCF sampling points is that there is no clear evidence that shading reduces CH$_3$Br emissions.

The air temperatures and enclosure temperatures were comparable for the non-shaded and shaded enclosures at OCF1–5. Although the difference in CH$_3$Br emissions between the non-shaded and shaded enclosures at OCF1 and OCF2 was greater than the variation in daily CH$_3$Br emissions observed during daylight hours on 04/08/2008 (Chapter 3), it is unlikely that shading resulted in the observed increase in CH$_3$Br emissions. It is more likely that the increased emissions were a result of intrinsic variation in the CH$_3$Br emissions at OCF1 and OCF2.
4.3.4 Shading studies at Red Moss of Balerno

The shading experiments were performed at the RMB sampling points on 10/07/2009. The CH\textsubscript{3}Br and CH\textsubscript{3}Cl fluxes for shaded and non-shaded enclosures are presented in Figure 4.11.

![Figure 4.11: Shading experiments for CH\textsubscript{3}Br (a) and CH\textsubscript{3}Cl (b) fluxes at RMB1-8. Bars represent the analytical uncertainty in CH\textsubscript{3}X flux.](image)

The only significant differences in CH\textsubscript{3}X fluxes between shaded and non-shaded enclosures were observed for CH\textsubscript{3}Cl emissions from RMB1, RMB3 and RMB6, Figure 4.11 (b). There were no significant differences in CH\textsubscript{3}Br emissions between non-shaded and shaded enclosures at any of RMB1–4, Figure 4.11 (a).
A 30 minute shaded enclosure was performed at RMB2 and RMB8 in the event that 10 minutes was insufficient time for the effects of shading to become apparent. However, the outcome of increased shading time was not clear. The CH$_3$Br emissions at RMB2 were not significantly different between non-shaded and 30 minute shaded. At RMB8 the only significant CH$_3$X flux was observed after 30 minutes shading.

The differences in CH$_3$Cl emissions between the non-shaded and shaded enclosures at RMB1, RMB3 and RMB6 were not consistent. At RMB1 and RMB6 the CH$_3$Cl emissions were greater during the non-shaded enclosure, but at RMB3 higher emissions were observed during the shaded enclosure. However, these differences were of the same magnitude as the daily variation in CH$_3$Cl emissions from RMB1–3 observed on 15/08/2008 (Chapter 3). Thus the significant increases and decreases observed between non-shaded and shaded enclosures at RMB1, RMB3 and RMB6 could represent ‘normal’ daily variation in CH$_3$Cl emissions.

4.3.5 Shading studies at St Margaret’s Marsh

The shading experiments were performed at the SMM sampling points on 08/07/2009. The CH$_3$Br and CH$_3$Cl fluxes for shaded and non-shaded enclosures are presented in Figure 4.12.
Figure 4.12: Shading experiments for CH$_3$Br (a) and CH$_3$Cl (b) fluxes at SMM1-4. Bars represent the analytical uncertainty in CH$_3$X flux.

At the SMM sampling points the shaded enclosures did not have a consistent effect on the CH$_3$Br emissions (Figure 4.12 (a)) and there was no significant effect on the CH$_3$Cl emissions (Figure 4.12 (b)). There were significant differences in CH$_3$Br emissions between non-shaded and shaded enclosures at SMM2–4. At SMM2 CH$_3$Br emission was greater during the 10 minutes shaded enclosure compared with the non-shaded enclosure and greater again during the 30 minute shaded enclosure. At SMM3 the CH$_3$Br emission was also greater during the shaded enclosure compared with the non-shaded enclosure. However, at SMM4, CH$_3$Br emissions decreased after 10 minutes shaded enclosure compared with the non-shaded enclosure. During the 30 minute shaded enclosure the CH$_3$Br emissions were significantly greater than the non-shaded enclosure.

The differences in CH$_3$Br emissions from SMM2–4 between the shaded and non-shaded enclosures could not be attributed to temperature which only varied between 1–2°C between shaded and non-shaded enclosures. It was also noted that the difference in CH$_3$Br emissions between shaded and non-shaded enclosures was much greater than daily variation in CH$_3$Br emissions from the SMM sampling points observed on 08/08/2008, Chapter 3. However, it is unlikely that the shaded enclosures are directly resulting in increased CH$_3$Br emissions at SMM, particularly since no correlation between CH$_3$Br emissions and light intensity was observed,
Section 4.2.4. It is more probable that the differences in CH$_3$Br emissions between shaded and non-shaded enclosures arise from variation in CH$_3$Br emissions on the day of sampling.

4.3.6 Summary

The effect of the shading experiments on CH$_3$Br and CH$_3$Cl fluxes was inconsistent across the sampling points. Although significantly lower emissions were observed at certain sampling points during the 10 (or 30 minute) shaded enclosure, at other sampling points CH$_3$X emissions actually increased after the shaded enclosure or were not observed to be significantly different from the non-shaded enclosure. It is therefore likely that any differences in CH$_3$Br emissions between shaded and non-shaded enclosures are due to intrinsic variation in the CH$_3$X emissions from a particular sampling point on the day of sampling.

The differences between shaded and non-shaded enclosures at ACM, OCF and SMM were greater than the variation in CH$_3$X fluxes observed during the diurnal studies. However, it is important to note that both the shading studies and the diurnal studies were conducted over a single day and at different times during the growing season. Both studies therefore represent a snapshot of CH$_3$X fluxes and may not fully capture the short-term variation in CH$_3$X fluxes.

Further field studies in which the effect of light intensity is examined in situ would be relevant for ecosystems in which CH$_3$X fluxes have been linked to light intensity as a possible driver, e.g. CH$_3$Cl emissions from RMB, Section 4.2.3. To elucidate the effect of reduced light intensity in shading experiments it would be important to compare shaded and non-shaded enclosures on several occasions over several days to fully characterise short-term variation in CH$_3$X fluxes. In addition it would also be useful to reverse the order of the shaded and non-shaded enclosures i.e. perform the shaded enclosure before the non-shaded enclosures.
4.4 Controlled experiments with *P. australis*

The vegetation removal experiments in this study (Chapter 3) indicated that uptake and emission processes occurred simultaneously at many of the sampling points where the plants are a source of CH$_3$X and the soils a small sink of CH$_3$X. However, only net CH$_3$X fluxes were measured in the field and as previously discussed (Section 4.2), it is intrinsically difficult to determine how CH$_3$X fluxes are affected by individual environmental parameters e.g. temperature and light, from *in situ* field studies. To address this issue the effect of air temperature, light intensity and soil moisture on the CH$_3$X fluxes from soil cores (RMB and SMM) and greenhouse grown *P. australis* were investigated under controlled conditions.

There have been a limited number of studies where CH$_3$X fluxes have been measured from plants in controlled conditions. Previous work has investigated CH$_3$X fluxes from greenhouse grown mangroves where the plants were successfully grown in an artificial growth medium (*Manley, et al.*, 2002). Although the effects of light intensity and temperature were not investigated, these parameters were controlled using a supplemental lighting source and a greenhouse where the temperature was controlled via a computer. CH$_3$X fluxes from rice have also been investigated in controlled greenhouse experiments (*Redeker and Cicerone*, 2004) where the water management practices were regulated.

The aim of this experiment was two-fold. Firstly, CH$_3$X fluxes from *P. australis* were investigated in isolation from soil-based fluxes to establish the gross plant-based production for this species. Secondly, the effect of external environmental parameters (PAR, ‘soil’ moisture and air temperature) on net CH$_3$X production from *P. australis* was studied.

4.4.1 Experimental set-up

*P. australis* were selected for the controlled experiments because they were demonstrated to be high emitters of CH$_3$Br (Chapter 3). The reeds were also a good system to use in these experiments because they are a fast growing annual plant and can be grown in a soil substitute. In March 2008 *P. australis* rhizomes of at least 150
mm in length and with at least 3 buds were collected from three locations at SMM. The rhizomes were washed, rinsed with deionised water and stored at 4°C in the dark until planting. Eighteen pots of 0.043 m³ in volume were filled with sand and a slow-release fertiliser (nitrogen/phosphorus/potassium ratio = 24:8:16). The pots were placed in trays and three rhizomes were planted 100 mm below the sand surface in 16 of the pots with two pots left as blanks. The *P. australis* were grown in a non-temperature controlled greenhouse where they were watered daily. A fertiliser solution containing the necessary trace elements and NPK (nitrogen/phosphorus/potassium ratio = 24:8:16) was applied twice a week.

An initial investigation during the 2008 growing season found the greenhouse grown *P. australis* to be active for CH$_3$X fluxes and sand-only blank pots to be inactive for CH$_3$X fluxes. The controlled study was performed from August 2009–September 2009 after the *P. australis* had grown sufficiently over the summer. Three different conditions which altered the temperature, light and moisture environment of the *P. australis* were compared with the ‘normal’ condition. At the ‘normal’ condition, pots were in the non-temperature controlled greenhouse at an average air temperature of 17°C. The light intensity was altered to give the ‘shade’ condition by covering the vegetation with green shading material (Section 4.2), shown in Figure 4.13 (a). The ambient temperature was increased to a minimum of 21°C by transferring the pots to a temperature controlled green house, Figure 4.13 (b), to give the ‘warm’ condition. The ‘normal’, ‘shade’ and ‘warm’ pots were watered daily. To alter the moisture conditions, the ‘dry’ pots were not watered during the week, but did receive fertiliser solution during this time. The water content of the sand growing medium was measured at the weekly sampling event using a Theta Probe (Delta T Devices Ltd., Cambridge, UK) calibrated to the sand growing medium.

Four replicate pots were subjected to a single condition (‘warm’, ‘shade’, ‘dry’ or ‘normal’) for a week, at the end of which the CH$_3$X fluxes were measured, Figure 4.13 (c). After sampling, the pots were rotated to the next condition so that the four replicate pots experienced each condition over a four week period. By rotating the replicates around the four conditions any external variation related to time and any systematic differences between the replicate groups could be accounted for.
4.4.2 Sample collection

To collect an air sample the pots, including the two blanks, were enclosed in a 0.1 m$^3$ chamber for 10 minutes between 08:00–13:00, Figure 4.13 (c). The air temperature and enclosure temperature were recorded at the time of sampling. The PAR and total solar radiation were recorded in the greenhouse during the month-long experimental period.

![Shaded P. australis](image)

Figure 4.13: The ‘normal’, ‘shaded’ and ‘moisture’ pots in the non-temperature controlled greenhouse (a); ‘temperature’ pots in the 21°C green house (b) and the chamber enclosure method (c).
After the enclosure a 500 mL air sample was withdrawn using a gas-tight syringe and transferred to a 1 L Tedlar bag. The samples were analysed using the GC-ECD, Chapter 2. Ambient air samples were collected from the non-temperature controlled greenhouse and the 21°C greenhouse at the time of sampling. After the four week experimental period all the above-surface vegetation was cut then weighed to determine the fresh weight per pot. The vegetation was dried at 70°C until constant weight. The CH$_3$X fluxes were expressed as ng g$^{-1}$ fresh weight h$^{-1}$ to account for variation in plant biomass between the pots.

4.4.3 Results

The total of 16 CH$_3$X flux measurements made at each condition (‘normal’, ‘warm’, ‘shade’ and ‘dry’) over the four week period were averaged and are compared in Figure 4.14.
The results presented in Figure 4.14 (a) show that the CH$_3$Br emissions tended to be higher in the ‘normal’ environment compared with the ‘shade’, ‘warm’ and ‘dry’ pots. On average CH$_3$Cl emission was observed under ‘normal’, ‘shade’ and ‘dry’ conditions, but CH$_3$Cl uptake was observed under ‘warm’ conditions, Figure 4.14 (b). However, single factor ANOVA showed that there was no significant difference in the CH$_3$Br or CH$_3$Cl fluxes between the different conditions.

Although the *P. australis* plants grown in this experiment were physically smaller than wild *P. australis* at SMM, the CH$_3$Br and CH$_3$Cl emissions from the greenhouse plants (normalised to fresh weight) were generally within the range of fluxes observed...
from the wild *P. australis* at SMM. These observations indicate that the greenhouse *P. australis* were behaving similarly to wild *P. australis* with respect to CH$_3$X production and therefore any results observed in this study are relevant to natural reedbed systems.

### 4.4.3.1 Variation in CH$_3$Br fluxes from *P. australis*

The variation in the CH$_3$Br fluxes between the individual pots within the replicate groups from week to week made it difficult to distinguish any differences in CH$_3$Br fluxes that may have been due to environmental conditions. The variation in the CH$_3$Br fluxes from the 16 individual pots is illustrated in Figure 4.15.

![Figure 4.15: CH$_3$Br fluxes from individual pots measured at weekly intervals. Replicate groups of four pots are shown as open circles (- - o - -), crosses (- - x - -), triangles (- - ▲ - -) and squares (- - ■ - -).](image)

It can be seen that the magnitude of the CH$_3$Br emissions from the individual pots within a replicate group of four was very different, for example the CH$_3$Br emissions from pot 14 were consistently higher (25 ng g$^{-1}$ h$^{-1}$ – 75 ng g$^{-1}$ h$^{-1}$) than the emissions from any of the other pots, Figure 4.15. In addition, the four replicate pots did not follow the same trends over the four week period despite being subject to the same conditions.

### 4.4.3.2 Experimental challenges

A complication in this experiment was the difficulty in controlling the environmental conditions, particularly air temperature and growth substrate moisture. The *P.
*australis* plants may have experienced less difference in the environmental conditions than intended. The temperature and PAR for the ‘normal’ and ‘shade’ conditions in the uncontrolled greenhouse are shown in Figure 4.16 (a–b) from 22/08/2008–30/08/2008. The average weekly volumetric water content of the sand growing medium for the 12 pots at ‘normal’ water content and at the ‘dry’ condition is shown in Figure 4.16 (c).
Figure 4.16: Temperature (a) and PAR (b) monitored in the uncontrolled greenhouse from 22/08/2008–30/08/2008. Average weekly volumetric water content of the sand growing medium for the 12 pots at normal water content and for the four ‘dry’ pots (c).
The temperature in the non-temperature controlled greenhouse varied according to the daily solar cycle and the average daily temperature decreased during the four week experimental period, Figure 4.16 (a). From mid- to late-August the peak daytime temperatures in the non-temperature controlled greenhouse sometimes exceeded the regulated temperature in the 21°C greenhouse. The temperature in the 21°C greenhouse probably exceeded this temperature too as the greenhouse was not actively cooled to keep the temperature at 21°C. The average temperature in the non-temperature controlled greenhouse was 17.2°C, making this greenhouse cooler overall compared with the 21°C greenhouse.

The PAR incident on the shaded *P. australis* was consistently reduced by 80% compared with the non-shaded *P. australis* pots, Figure 4.16 (b).

The average volumetric water content of the four ‘dry’ pots was compared with the average volumetric water content of the remaining 12 pots experiencing ‘normal’ moisture conditions that week. The volumetric water content was consistent for the pots experiencing ‘normal’ moisture conditions over the experimental period, but the volumetric water content of the ‘dry’ pots was not consistent during the experimental period and was significantly below the ‘normal’ moisture conditions only on 29/08/09 and 12/12/09.

**4.4.3.3 Summary of CH$_3$X fluxes from greenhouse grown *P. australis***

The absence of any effect of reduced PAR and moisture conditions on CH$_3$X fluxes from greenhouse grown *P. australis* is in agreement with the field observations. The results presented in Section 4.2.4 showed no correlation between PAR intensity or soil water level and CH$_3$X flux. However, the field data did show a significant and positive correlation between air temperature and CH$_3$Br emission. It is possible that the average temperature of 21°C in the controlled greenhouse was too warm for the *P. australis* plants and resulted in a stress situation which reduced CH$_3$Br emissions. To extrapolate these findings to other wetland sites where CH$_3$X fluxes sporadically coincide with PAR, controlled studies with vegetation from other wetland sites would need to be investigated.
4.5 Controlled experiments with soil cores from SMM and RMB

CH₃X fluxes from two wetland soils were investigated in this study. Soil from the SMM wetland site was selected to complement the controlled *P. australis* experiments and provide a more complete picture of CH₃X fluxes from the SMM wetland system. Peat cores from the RMB wetland site were investigated in this experiment as the peat had high organic matter content and a naturally low pH of <4; conditions that have been identified by Keppler *et. al.* (2000) as conducive to producing CH₃X via geochemical reactions.

As for the controlled experiments with *P. australis*, the aim of the controlled soil core experiments was two-fold. Firstly, the net CH₃X flux from the soil component of two wetland ecosystems was investigated in isolation to gauge the contribution of the soil component to the net fluxes from a sampling point. Secondly, the effect of soil moisture and temperature was studied to determine if these two parameters directly affected the soil-based CH₃X fluxes.

4.5.1 Experimental set-up

Soil cores of 200 mm in diameter and 150 mm in depth were removed from SMM and RMB on 06/05/09 and 07/05/09. Six soil cores were taken from each of RMB and SMM and transferred to water-tight, black polythene bags of approximately the same diameter as the cores to maintain the integrity of the cores. Extra soil and peat samples were removed from SMM and RMB on the same day to be analysed for gravimetric water content (Chapter 2). The soil cores, inside the polythene bags, were stored in 0.012 m³ buckets. The cores were weighed regularly and the core water content was maintained by the addition of an appropriate volume of water when necessary. The CH₃X fluxes from the soil cores were measured at different temperature and moisture conditions to determine if these parameters affect CH₃X fluxes from soil cores. The effect of different light conditions was not investigated as light levels were not expected to influence CH₃X fluxes from soils.
4.5.1.1 Temperature controlled experiment

The temperature controlled study was performed at 12.5°C and 20°C. Three cores from each of RMB and SMM were kept at ~20°C in the laboratory and the remaining three cores from each wetland were kept outside in the shade at an average temperature of 12.5°C. After one week the cores were analysed for CH$_3$X fluxes and then the soil cores were switched so that the cores at 20°C were moved outside and the outside cores were moved into the laboratory. The respective cores were maintained at 12.5°C or 20°C for a further week and then analysed again for CH$_3$X fluxes.

4.5.1.2 Moisture controlled experiment

Earlier experiments with cores from RMB and SMM demonstrated that the moisture conditions of the soil, or peat, were more difficult to control than the temperature. The soil cores could be air-dried over time to reduce the water content, but it was difficult to increase the core water content by adding water to the cores. For this study three of the cores from each site were maintained at the initial water content of 92% and 77% for the RMB and SMM cores respectively. The remaining three cores from RMB were air-dried to 75% water content and the remaining three cores from SMM were air-dried to 65% water content. The ‘normal’ and ‘dried’ cores from RMB and SMM were maintained at the stated water content for one week and then analysed for CH$_3$X fluxes. To account for time effects and variation between the soil cores the three ‘normal’ cores from RMB and SMM were then dried to 75% and 65% respectively and the ‘dry’ cores were re-hydrated back to the original water content by gradually adding water to the core. When the re-hydrated soil cores and dried soil cores reached the appropriate water content they were analysed for CH$_3$X fluxes.

4.5.1.3 Sample collection from soil and peat cores

To collect an air sample the cores were enclosed in the 0.012 m$^3$ buckets for 10 minutes using an air-tight lid fitted with a three way tap, Figure 4.17. A 500 mL air sample was withdrawn with a gas-tight syringe and transferred to a 1 L Tedlar bag.
The air samples were analysed using the GC-ECD as described in Chapter 2. The air temperature and the core temperature were recorded at the time of sampling. The CH$_3$X fluxes were calculated in ng m$^{-2}$ h$^{-1}$, i.e. normalised to the surface area of the core which was 0.031 m$^2$.

4.5.2 Results

4.5.2.1 Temperature controlled soil core studies

The average CH$_3$X flux at each temperature condition was calculated for the RMB and SMM cores from the total of six measurements at each condition, Figure 4.18.
There was no consistent trend in CH$_3$X fluxes from RMB and SMM cores stored at 12.5°C and 20°C. At 12.5 °C the CH$_3$Br fluxes were low and variable with both uptake and emission of CH$_3$Br being observed from RMB and SMM cores. There was less variation in CH$_3$Br fluxes from the RMB and SMM soil cores at 20°C, with low rates of uptake observed at all cores from both sites. Low rates of CH$_3$Cl uptake were consistently observed from all SMM and RMB cores at 12.5°C, but at 20°C uptake and emission of CH$_3$Cl was observed at RMB and SMM cores. Single-factor ANOVA showed no significant difference between CH$_3$Br and CH$_3$Cl fluxes at 12.5°C and 20°C.
4.5.2.2  Moisture controlled soil core studies

The average $\text{CH}_3\text{X}$ flux at each moisture condition was calculated for the RMB and SMM cores from the total of six measurements at each condition, Figure 4.19.

![Figure 4.19: CH$_3$X fluxes from RMB (a) and SMM (b) cores at different moisture conditions. Symbols represent; CH$_3$Br fluxes, ($\circ$) and CH$_3$Cl fluxes, ($\square$). Bars represent the SEM, $n = 6$ for CH$_3$Br and $n = 3$ for CH$_3$Cl.]

The results presented in Figure 4.19 (a) show that the RMB peat cores took up CH$_3$Br at 92% and 75% water content. Single-factor ANOVA found that there was no significant difference in the uptake rate between cores at 92% and 75% water content. It is therefore not possible to ascribe peat moisture as a driver of CH$_3$Cl or CH$_3$Br fluxes from RMB peat cores. The comparatively high CH$_3$Cl emission from the RMB cores at 92% water content was driven by a large, isolated CH$_3$Cl emission event observed at a single core. Significant CH$_3$Cl flux at 92% water content was only observed from one other RMB core which emitted CH$_3$Cl at a very low rate.
There was no consistent trend in the CH$_3$X fluxes from the SMM soil cores at 77% and 65% water content, although all cores were less active and demonstrated more variation in CH$_3$X fluxes at 65% water content compared with 75% water content, Figure 4.19 (b). Low rates of CH$_3$Br uptake were observed from SMM soil cores at 77% water content, but at 65% water content, uptake and emission of CH$_3$Br was observed. Single-factor ANOVA found no significant difference between the CH$_3$Br fluxes from SMM at the different water contents.

The large CH$_3$Cl emission event from one RMB core was unexpected and the isolated nature of this measurement means it is difficult to speculate on its origin. CH$_3$Br production has been observed in soils, but it is not generally the dominant process (Varner, et al., 2003). If the emission event was a true measurement the possible sources could include fungal processes, abiotic process or some previously unidentified source. The size and uniqueness of the emission means it is unlikely to be an abiotic source as this would be expected to be constant over the study period. Fungi have been shown to emit CH$_3$Cl in larger amounts towards the end of their life cycle (Harper, et al., 1989) and if there was a fungal population associated with this particular core, it could have resulted in the observed CH$_3$Cl emissions.

4.5.2.3 Summary of CH$_3$X fluxes from soil cores

The results from the temperature and moisture controlled experiments showed that these parameters did not significantly affect the CH$_3$X fluxes from RMB and SMM soil cores. In fact, the CH$_3$X fluxes from the soil cores were more variable within a site than at different temperature and water conditions. These experiments further demonstrate the heterogeneity of CH$_3$X fluxes within a system and the difficulty of trying to isolate the effects of different environmental conditions. The CH$_3$Br and CH$_3$Cl fluxes from RMB peat and SMM soil were very low, demonstrating that the soil (or peat) component of these wetland systems is not a major contributor to net flux from the atmosphere. Because these fluxes were very low, it may have been beneficial to use a longer enclosure time to determine the fluxes more accurately.
The lower temperature (12.5°C) condition in this experiment represented field conditions in early and late summer at SMM and RMB, Figure 4.5 and Figure 4.7, whereas the 20°C temperature condition was higher than generally recorded at either sampling site. Previous laboratory based studies have suggested that CH\textsubscript{3}Br uptake by soils is a temperature dependant process (Hines, et al., 1998). However, this study was performed using above-ambient CH\textsubscript{3}Br concentrations and small soil samples; conditions which may not accurately represent CH\textsubscript{3}X flux processes in the RMB and SMM soils. Where more realistic whole soil systems have been studied, for example shortgrass steppe soils and Alaskan tundra soils (Teh et al., 2008, Rhew et al., 2008) the results have been conflicting. CH\textsubscript{3}Br and CH\textsubscript{3}Cl uptake was not dependant on temperature in shortgrass steppe soils (Teh, et al., 2008), but temperature was found to be a secondary driver for CH\textsubscript{3}X uptake in Alaskan tundra soils (Teh, et al., 2009). Together with the results presented in this study, these investigations show that the effect of temperature on CH\textsubscript{3}X fluxes from soils is likely to be site specific.

The absence of any observable effect of temperature on CH\textsubscript{3}X fluxes from soils means that any inter-seasonal variation in soil temperature is not likely to affect CH\textsubscript{3}X. Intra-seasonal variation in soil temperature at the wetland sites was generally very small, Section 4.2. Further, any average overall increase in soil temperature in a warmer climate is unlikely to affect CH\textsubscript{3}X fluxes from wetland soils.

Hydrological regulation has been more consistently identified as a driver of CH\textsubscript{3}X fluxes. Studies in shortgrass steppe soils (Teh, et al., 2008) and Alaskan tundra soils (Teh, et al., 2009) have found that CH\textsubscript{3}X uptake is greater in drier conditions. These findings are in contrast to the results in this study, but the temperate grassland soils and shortgrass steppe soils were much drier than the soils from SMM and RMB, and may not represent the CH\textsubscript{3}X processes occurring in these wetland ecosystems. The water conditions in this experiment represented the ambient conditions at the time of sampling and a drier condition. For RMB, the ‘dry’ condition (75% water content) was probably much drier than the bog would ever be naturally. However, the results show that significant drying of a peat bog, for example by draining, would probably have little impact on CH\textsubscript{3}X fluxes from the peat itself. The dry condition for the SMM soil cores (65% water content) was within the range of naturally occurring moisture conditions at SMM (Chapter 3).
4.6 Summary of the effects of environmental parameters on CH$_3$X fluxes from wetlands

The results in this chapter compared CH$_3$X fluxes in four Scottish wetlands with external environmental parameters including light intensity, air temperature, soil temperature and soil water level. This was done to determine if any of these parameters was directly driving CH$_3$X fluxes. At sampling sites where the CH$_3$X emissions followed a defined seasonal cycle, the seasonal emission trends generally corresponded to seasonal trends in temperature and/or light intensity. Comparison of the intra-seasonal variation in the environmental parameters and the CH$_3$X fluxes, together with the controlled greenhouse experiments indicated that there was no strong evidence that environmental conditions directly affected CH$_3$X fluxes.

**Temperature and light intensity as seasonal drivers of CH$_3$X fluxes:**

The air temperature and PAR intensity appeared to act as drivers for the onset of CH$_3$X emissions from ACM4, OCF1–4 and RMB1–4 (except CH$_3$Br at RMB4). At these sampling points the increasing air temperature and PAR at the start of the growing season corresponded well with increasing CH$_3$Br and CH$_3$Cl emissions. Towards the end of the growing season declining air temperatures and PAR intensity corresponded with declining CH$_3$Br and CH$_3$Cl emissions. It is difficult to ascribe one or other of temperature or PAR as the driver for CH$_3$X emissions as both of these parameters followed very similar seasonal trends. Indeed it may not be relevant to do so, as the plants respond to increases in both parameters at the start of the growing season.

In contrast to the other sampling points where plant-based CH$_3$X emission was the dominant process, at the SMM sampling points soil temperature, rather than air temperature and PAR intensity was the driver for seasonal CH$_3$Br emissions. This observation reflects the nature of the *P. australis* growth cycle which originates from rhizomes below the ground surface.

At ACM1–3 and RMB4 (CH$_3$Br only), where CH$_3$X uptake was the dominant process, the seasonal patterns in uptake did not correspond so well with the seasonal
patterns in temperature and light intensity. Significant CH$_3$Br and CH$_3$Cl uptake was only observed once temperature (air and soil) and light intensity had reached peak growing season levels. Uptake processes continued at a lower rate into the winter months after temperature and light intensity had declined to winter minimum values. It is most likely temperature that drives the initiation of uptake processes in the summer. However, the observation of uptake processes during the winter suggests that warm summer soil temperatures are not an essential requirement.

The varying response of the CH$_3$X fluxes to the seasonal trends in the environmental parameters highlights that the processes leading to CH$_3$X flux are system specific and that overarching descriptions of the effect of environmental parameters cannot be made.

*Environmental parameters did not directly affect CH$_3$X fluxes:*

The long-term datasets of CH$_3$X fluxes and environmental parameters showed that intra-seasonal variation in temperature, light intensity and soil water level did not drive intra-seasonal variation in CH$_3$X fluxes. An exception was the CH$_3$Cl emissions from RMB1–3 where emission peaks coincided with air temperature peaks and PAR peaks during the 2008 growing season. Field-based shading experiments together with controlled experiments using greenhouse grown *P. australis*, and soil cores from RMB and SMM, also failed to identify any direct correlation between CH$_3$X fluxes and environmental parameters. The controlled greenhouse and laboratory experiments did highlight the inherent variability in CH$_3$X fluxes from the same type of vegetation and soil within a site.

*Implications for proposed flux mechanisms:*

At ACM4, OCF1–5 and RMB1–4 the CH$_3$X emissions (no CH$_3$Br emission at RMB4) were identified as being of plant origin (Chapter 3), although the production mechanisms were probably not primary metabolic processes. The observation that CH$_3$X emissions are dependant on temperature (air or soil) and/or PAR intensity to kick-start emissions at the start of the growing season supports this theory. The absence of direct correlation between CH$_3$X fluxes and environmental parameters suggests that either the plants or the processes leading to CH$_3$X emission and uptake are insensitive to variation in temperature and light once they are active for the
growing season. This could indicate that the magnitude of CH₃X emission is controlled by production mechanisms and transport process rather than production mechanisms alone. Transport, rather than production was suggested as the rate limiting step for CH₃X uptake in temperate peatlands (White, et al., 2005) and Arctic tundra (Teh, et al., 2009).

**Implications for future CH₃X emission trends:**

A possible implication for future trends in CH₃X fluxes is that emissions which follow seasonal trends linked to increasing air temperatures and PAR could begin earlier if the onset of the growing season is brought forward as a result of a warmer climate. Thus more CH₃X could be emitted to the atmosphere during a growing season. However, if it is the light intensity rather than temperature which is driving the onset of emissions, a longer growing season would have no effect. A longer growing season may also increase the net uptake of CH₃X in systems such as ACM, thus partially counteracting any increases in CH₃X emission.

The absence of any direct correlation between CH₃X fluxes and water level suggests that wetland drainage alone may not alter the CH₃X fluxes. However, any vegetation changes and/or land-use changes that would likely be associated with drainage would affect the net CH₃X flux to the atmosphere.

The results presented in this study do suggest that to make accurate predictions of future CH₃X fluxes and to understand what is driving variation of CH₃X fluxes within a system, it is important to understand what the processes are that lead to net flux within a system.