Growing season methyl bromide and methyl chloride fluxes at a sub-arctic wetland in Sweden

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[1] Methyl bromide and methyl chloride fluxes were measured at several sites in a sub-arctic wetland near Abisko, Sweden (68°28′N 18°49′E) throughout the 2008 growing season. Averaged over 92 flux measurements the sub-arctic wetland was found to be a small net sink for CH_3Br, with mean (±1 sd) uptake of -25 (±20) ng m^{-2} h^{-1}, but a small net source of CH_3Cl with mean emissions of 400 (±1600) ng m^{-2} h^{-1}. Seasonal trends were observed in both CH_3Br and CH_3Cl net fluxes, but diurnal trends for CH_3Cl only, with peak emissions observed during the afternoon. CH_3Cl fluxes differed significantly with hydrological status of measurement locations; however, no other substantial correlations were observed between fluxes and external parameters (air and soil temperature and PAR). This study shows that the single previous estimated sink flux for CH_3Cl in tundra globally (derived from measurements in Alaska) requires revision, although not that for CH_3Br. **Citation:** Hardacre, C. J., E. Blei, and M. R. Heal (2009), Growing season methyl bromide and methyl chloride fluxes at a sub-arctic wetland in Sweden, *Geophys. Res. Lett.*, *36*, L12401, doi:10.1029/2009GL038277.

1. Introduction

[2] The natural sources and sinks of methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) are poorly constrained due to inherent difficulty in obtaining temporally and spatially representative data in heterogeneous natural systems. These gases transport halogen atoms into the upper atmosphere and as emissions of man-made halogen-containing source gases become subject to control, natural fluxes of CH_3Br and CH_3Cl are becoming increasingly important contributors to stratospheric ozone loss processes. It is estimated that by 2100 CH_3Br and CH_3Cl will together contribute approximately 50% of the equivalent effective stratospheric chlorine (EESC) [*World Meteorological Organization* (*WMO*), 2007], where EESC is a parameter that quantifies the potential for stratospheric ozone depletion for all Cl and Br-containing gases, adjusted to account for the different atmospheric lifetimes of different gases and the substantially greater ozone depletion by Br compared with Cl [*Newman et al.*, 2007; *WMO*, 2007]. Nearly all natural terrestrial systems thus far investigated have been found to have some role, to greater or lesser extent, on methyl halide fluxes. Consequently, considerable uncertainties remain in constraining terms in the global budgets for CH_3Br and CH_3Cl [*WMO*, 2003, 2007].

[3] Temperate wetlands and peatlands are among the established natural sources of CH_3Br and CH_3Cl [*Varner et al.*, 1999; *Dimmer et al.*, 2001]; however global flux estimates for wetlands are based on only a few studies in temperate locations. Wetlands and peatlands are vulnerable to land-use change and potentially to climate change also. High-latitude wetlands, in particular, are already being affected by warmer temperatures with reduced permafrost observed in some locations [*Berner et al.*, 2005].

[4] Although high-latitude wetlands are not anticipated to be a major source or sink of CH_3Br or CH_3Cl, it is important that CH_3Br and CH_3Cl fluxes from these areas are quantified in order to constrain CH_3Br and CH_3Cl budgets and to make predictions about future flux patterns in a changed climate. Data for CH_3Br and CH_3Cl fluxes at polar latitudes have been reported previously only for arctic Alaskan tundra [*Rhew et al.*, 2007; *Teh et al.*, 2009], and did not include measurements over the full growing season.

[5] Seasonal and diurnal trends in CH_3Br and CH_3Cl fluxes from non-polar ecosystems have been reported in a number of studies [e.g., *Redeker et al.*, 2000; *Rhew et al.*, 2002; *White et al.*, 2005; *Drewer et al.*, 2006; *Manley et al.*, 2006], but there has been no consistent evidence for external parameters driving CH_3Br or CH_3Cl fluxes across all ecosystem types; individual studies have suggested that light [*Drewer et al.*, 2006], temperature [*Rhew et al.*, 2000, 2002; *Redeker and Cicerone*, 2004], or soil pore-water saturation [*Redeker and Cicerone*, 2004] may affect emissions. In arctic Alaskan tundra it was found that drained sites had greater rates of CH_3Br and CH_3Cl uptake than flooded sites in both coastal and inland areas [*Rhew et al.*, 2007; *Teh et al.*, 2009], with water table depth correlating most strongly with CH_3Cl and CH_3Br net uptake [*Teh et al.*, 2009].

[6] In this study, CH_3Br and CH_3Cl fluxes were measured at a number of sites in sub-arctic wetland near Abisko, Sweden throughout the 2008 growing season (June–September), including a number of intra-daily flux measurements. Data for external parameters including air temperature, ground temperature, chamber temperature and photosynthetically active radiation (PAR) were also collected.

2. Experiment

2.1. Sampling Sites

[7] Flux measurements were undertaken in sub-arctic wetland areas in the vicinity of the Abisko Scientific Research Station (ANS), Abisko, northern Sweden (68°28′N 18°49′E). An initial study was carried out in August 2007 (for CH_3Br only) and a longer, seasonal study

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was carried out from June to September 2008 to capture the sub-arctic growing season.

[8] In the initial set of measurements, in August 2007, air samples were collected from 15 sampling points situated within 5 different wetland locations. Four locations were 1.5 km south of ANS, at elevations between 420 and 440 m a.s.l. (average precipitation 304 mm p.a), whilst the fifth location was Stordalen Mire, 10 km east of ANS, at 360 m a.s.l. (average precipitation 400 mm p.a.). The sun was above the horizon between 18.5 and 20 hours per day during the two week sampling period and there was no complete darkness. The individual sampling points within a location were chosen to capture the differences in hydrology and vegetation at that location. Broadly these could be divided into wet areas, dry areas and damp areas. A summary of the major types of vegetation present in each category is given in Table 1.

[9] Regular two-weekly measurements were made throughout the full 2008 sub-arctic growing season (June–September 2008) at two of the locations 1.5 km south of ANS used in the initial study. There were six sampling sites in total, two each in areas designated as wet, damp and dry. The hours of daylight varied over the study period. Until 23 July the sun never set, thereafter declining to 15 h per day above the horizon by 4 September. However, even under clear-sky conditions sampling sites were not necessarily exposed to direct sunlight because of shadowing from surrounding mountains.

2.2. Sampling Methods

[10] At each sampling point a 400 mm diameter by 200 mm high PVC collar was sunk 150 mm into the ground and remained in place for the duration of the sampling campaign. To collect a flux sample an appropriately sized chamber was secured to the collar to create an airtight enclosure. In the initial study, either a 0.044 m^3 chamber or a Perspex sheet was used depending on the height of the vegetation within the collar. For the seasonal study, a 0.031 m^3 chamber was used. Chambers were sealed for 10 min after which a 500 mL sample was withdrawn by gas-tight syringe and transferred to an evacuated 1 L Tedlar bag. An ambient air sample was similarly collected. Bags were couriered to the University of Edinburgh for analysis. The ambient air temperature, sub-surface temperature at 5 cm depth and the internal chamber temperature, were recorded at each sampling event. Continuous measurements of PAR were available from the ANS weather station.

2.3. Analysis Methods

[11] The air samples were analysed for CH_3Br and CH_3Cl using an HP5890 gas chromatograph equipped with oxygen-doped electron capture detection and a ZB642 capillary column (Phenomenex Inc., Torrence, CA, USA) 30 m in length, i.d. 0.32 mm and 1.8 μm film thickness. A custom built, two-stage preconcentration unit was used prior to GC separation [Drewer et al., 2008]. The first trap was a 1/4 inch diameter by 100 mm long stainless steel tube filled with Tenax TA 60/80 mesh (Supelco, Bellefont, PA, USA). This was cooled to −30°C before sample loading using dual two-stage Peltier cells (Melcor, Trenton, NJ, USA). The second trap was a 1/8 inch diameter by 200 mm long stainless steel tube filled with fine glass beads and cooled

to −80°C using dry ice. A 100 mL sample aliquot was loaded onto the first trap and the trapped analytes subsequently transferred to the second trap using switching valves (VICI, Houston, TX, USA). After 5 min the second trap was flash heated to transfer the analytes onto the column. The temperature programme was 5 min at 40°C, ramping for 5 min at 40°C min^{-1} and hold for 5 min at 240°C.

[12] Calibration curves for CH_3Br and CH_3Cl were prepared weekly using dilutions of certified standards: 500 ± 10 ppbv CH_3Br in nitrogen (Air Products Inc.) and 15.8 ± 0.5 ppmv CH_3Cl in nitrogen (Air Liquide). Since a net flux is derived from difference between parallel enclosure and ambient samples, some sources of uncertainty subtract out, for example in primary standard concentrations and their dilutions in an individual calibration curve. The major uncertainty in an individual net flux value arises from the interpolations from a given calibration regression fit. This uncertainty was propagated with uncertainties in other relevant parameters, e.g., enclosure net volume, to derive an estimate of overall standard deviation in net flux value. Double these ±1 σ values were used to define the limits of detection for net flux from the field chambers, yielding values of ±21 and ±490 ng m^{-2} h^{-1}, for CH_3Br and CH_3Cl, respectively.

3. Results

[13] Figure 1 shows the time series of net CH_3Br and CH_3Cl fluxes during the 2008 growing season for those measurements made within the time period 10:00–16:30 on each occasion. These data constitute the first full-season time series of methyl halide fluxes at high latitude. Seasonal variation is apparent for both CH_3Br and CH_3Cl, with flux magnitudes changing most markedly through June and early July, corresponding to the most active period of the growing season, and smallest net fluxes at the beginning and end of the growing season.

[14] Figure 2 shows the net CH_3Br and CH_3Cl fluxes measured at four-hourly intervals over a 24 h period on 4th June from collars 'Wet 2', 'Dry 2' and 'Damp 1'. CH_3Br fluxes were very small during this sampling period and there was no significant diurnal flux trend for any of the three sites. In contrast, there was some diurnal variation in CH_3Cl fluxes, with a peak occurring around the middle of the day for all three sites investigated. Air temperature varied from a low of 8.9°C (averaged across sites) at 00:30 am to a high of 20.5°C at 16:30 pm and soil temperatures followed a similar cycle. The lag between peak temperature and peak CH_3Cl emissions is consistent with the paradigm of uptake and emission processes occurring simultaneously (see section 4). Peak emissions related to plant activity occur when there is most light, around midday, but as soil temperatures increase, bacterially-mediated uptake processes increase, reducing the net flux to the atmosphere.

[15] Aside from the diurnal cycle in net CH_3Cl flux noted above, no substantial correlations between CH_3Br or CH_3Cl flux and air temperature, chamber temperature, sub-surface temperature or PAR were discernible for the time-series data in this study. It is inherently difficult to tease out any such relationship(s), if they exist, from in situ field data due to

Table 1. Classification of Sampling Sites According to Hydrological Condition and Main Types of Vegetation Present

Water Conditions	Main Plant Species Present
Wet	*Carex rostrata*, bryophytes
Damp	*Equisetum palustre*, sphagnum mosses
Dry	*Vaccinium spp., Betula nana, Empetrum nigrum, Andromeda polifolia, Eriophorum spp., Rubus chamaemorus*, lichens, bryophytes

uncontrolled confounding between these factors (e.g., temperature and PAR) and with other factors (e.g., date during season and individual site characteristics).

[16] However, the magnitude of CH_3Cl fluxes did differ significantly (ANOVA) between locations classified according to their hydrology and vegetation (Figure 3). Mean CH_3Cl fluxes from each of the pairs of locations designated 'Wet', 'Damp' and 'Dry' were -160 ng m^{-2} h^{-1}, 1300 ng m^{-2} h^{-1} and 620 ng m^{-2} h^{-1}, respectively. These averaged values mask an important observation from Figure 1 (bottom) that locations classified as 'Dry' had the greatest seasonal range in fluxes, having generally greater net emission of CH_3Cl than other sites in the early part of the season, but greater net uptake of CH_3Cl in the latter part of the season. CH_3Br fluxes did not differ significantly with hydrology/vegetation classification, although there was a non-significant tendency for greater CH_3Br uptake at drier sites (Figure 1, top).

4. Discussion

[17] A seasonal variation in net CH_3Br or CH_3Cl fluxes, as observed here, was not reported by *Rhew et al.* [2007] for their coastal Alaskan arctic tundra sites, but their measurements only took place in late June and mid August.

[18] The sampling sites at Abisko were generally a net sink for CH_3Br. The mean (± 1 sd) net CH_3Br flux for the data shown in Figure 1 is -30 (± 25) ng m^{-2} h^{-1} ($n = 60$), with greatest net uptake coincident with the longest days in late June and early July. Including all flux measurements made during daylight hours between June and September at these sites yields an overall mean (± 1 sd) net CH_3Br flux of -25 (± 20) ng m^{-2} h^{-1} ($n = 92$). The similar mean fluxes for the full and subset of measurements is consistent with the interpretation that any diurnal variability is insignificant compared with variability on the week-to-week time scale and between sites. The small net uptake of CH_3Br observed at these high-latitude wetlands contrasts with the net emissions measured at wetland and peatland areas in Scotland (C. J. Hardacre, unpublished data, 2009), Ireland [*Dimmer et al.*, 2001] and New Hampshire, USA [*Varner et al.*, 1999] but is consistent with the net CH_3Br uptake reported for arctic Alaskan tundra [*Rhew et al.*, 2007; *Teh et al.*, 2009]. These latter studies reported average net CH_3Br flux of -18 ± 22 ($n = 40$) and -45 ± 60 ($n = 36$) ng m^{-2} h^{-1} (converting these authors' standard errors to standard deviations for comparison with presentation here).

[19] During the initial study at Abisko in August 2007, the mean (± 1 sd) net CH_3Br flux was -17 (± 17) ng m^{-2} h^{-1} ($n = 16$, data not shown). Comparing this with the average flux in August 2008 of -13 (± 19) ng m^{-2} h^{-1} ($n = 16$) shows there

was no substantive inter-annual variation in CH_3Br flux between these two years. In the Alaskan studies, the greater net uptakes of CH_3Br and CH_3Cl observed in 2006 than in 2005 was attributed to the higher soil temperatures in 2006 [*Rhew et al.*, 2007; *Teh et al.*, 2009].

[20] The seasonal pattern of CH_3Cl net fluxes at the Abisko sites was different to that of CH_3Br (Figure 1). Net emission of CH_3Cl was generally observed during the period early June to late July (except at collar 'Wet 2'), with more net uptake later in the season. Measurements on 11 Aug showed comparatively large uptake of CH_3Cl at all sites. There was no obvious reason to doubt the authenticity of these data. On average, net flux was positive: mean (± 1 sd) net CH_3Cl flux for the data shown in Figure 1 was 550 (± 1800) ng m^{-2} h^{-1} ($n = 60$), or 400 (± 1600) ng m^{-2} h^{-1} if all 92 measurements made during daylight hours are included. Again the comparable mean values demonstrate that seasonal and spatial differences dominate the flux variability. Likewise, the larger relative standard deviation in the CH_3Cl flux measurements compared with the CH_3Br flux measurements reflects the larger seasonal variation in the former than in the latter. The small net emission observed for CH_3Cl on average across 6 sites and the whole growing season at Abisko is consistent with observations of emissions, on average, in Scottish wetlands (C. J. Hardarcre, unpublished data, 2009) and Irish peatlands [*Dimmer et al.*, 2001] but in contrast to the average net CH_3Cl uptakes of -637 (± 610) ng m^{-2} h^{-1} [*Rhew et al.*, 2007] and -1240 (± 1350) ng m^{-2} h^{-1} [*Teh et al.*, 2009] reported for the
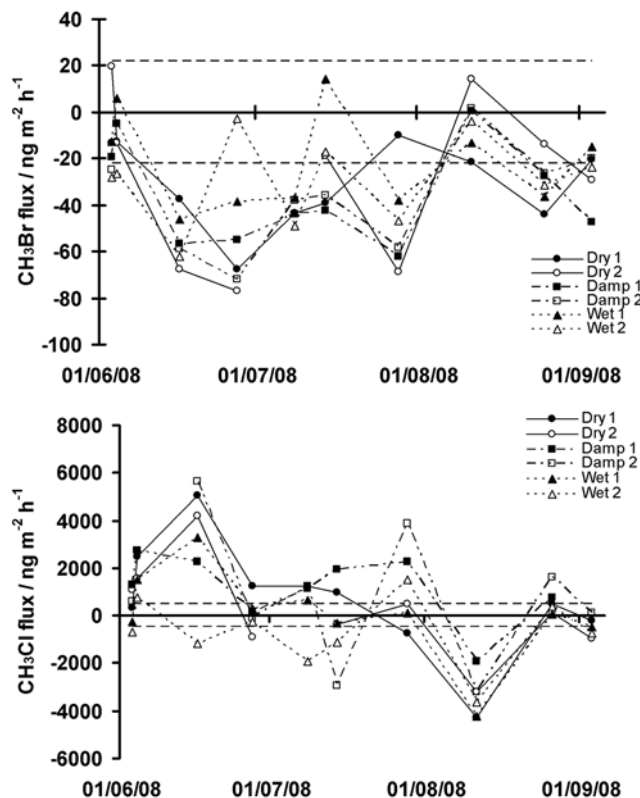

Figure 1. Time series of net CH_3Br and CH_3Cl fluxes from six sites during the 2008 growing season. Horizontal dashed lines indicate limits of detection for CH_3Br and CH_3Cl net flux determination.
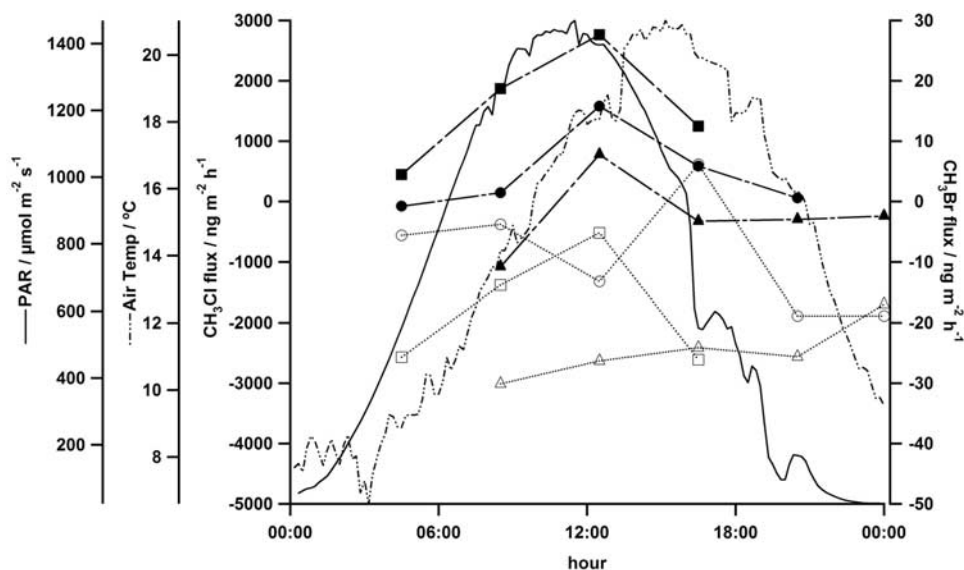
Figure 2. CH_3Br (open symbols) and CH_3Cl (solid symbols) fluxes from sites 'Wet 2' (circles), 'Dry 2' (squares) and 'Damp 1' (triangles), together with ambient air temperature and PAR, measured over a 24 hour period on 4 June 2008. Limits of detection for net flux determination are ± 21 ng m^{-2} h^{-1} and ± 490 ng m^{-2} h^{-1} for CH_3Br and CH_3Cl, respectively.

Alaskan tundra sites (again converting these authors' expressions of variability into standard deviations).

[21]   An association between hydrology and methyl halide fluxes has been reported previously. Both *Rhew et al.* [2007] and *Teh et al.* [2009] measured greater CH_3Br and CH_3Cl uptake at drier locations in their studies in Alaskan tundra, with the latter reporting that water table depth was the best predictor of both net and gross CH_3Br and CH_3Cl uptake. On the other hand, *Redeker and Cicerone* [2004] reported that low water conditions in rice paddies, another highly moist environment, enhanced net CH_3Br and CH_3Cl emission from certain rice cultivars. The current field study does not distinguish whether the difference in CH_3Cl (and CH_3Br) fluxes between sites was driven by the vegetation or the hydrological status, but it is likely that both are relevant as there was not a consistent trend in CH_3Cl flux from wet to dry soil conditions.

[22]   The picture that emerges from consideration of this study in Swedish high-latitude wetlands, and the studies in arctic Alaska [*Rhew et al.*, 2007; *Teh et al.*, 2009] and New Hampshire peatlands [*White et al.*, 2005] (together with further data from wetlands and peatlands in Scotland) is of land-atmosphere CH_3Br and CH_3Cl fluxes in such systems being the net resultant of plant- and soil-mediated emission and soil-mediated uptake; and that the relative magnitudes of each varies with micro-topology of the site (i.e., with vegetation and hydrology) and with time during the season. The latter factor impacts on vegetation activity and hydrology. Soils at the start of the season at Abisko are wetter than subsequently due to snow and ground-ice melt, so soil uptake rates are lower, yet plant-related activity is higher. The net flux is dynamically sensitive to changes in soil moisture and biological activity as the season progresses through to drier soils but cooler conditions and decreased vegetation growth. This picture is consistent with the observation by *Teh et al.* [2009] that the limitation on methyl halide uptake in saturated soils is due to mass transfer limitation rather than reduced microbial activity under anaerobic conditions. It also consistent with the suggestion that measurements of CH_3Cl fluxes which miss the beginning of the growing season in these ecosystems will likely show averaged net negative flux overall.

[23]   When comparing the results from this study site with those in Alaska [*Rhew et al.*, 2007; *Teh et al.*, 2009], it is also important to remember that the Abisko sites, although within the Arctic Circle, differ from the Alaskan sites not only biogeographically but in being classified as sub-arctic in terms of vegetation cover and climate rather than arctic. The warmer sub-arctic climate, and generally greater vegetation cover, appears to result in small net CH_3Cl emissions prevailing at Abisko when integrated over the full growing season and all sites, consistent with observations of net CH_3Cl emissions overall in other comparatively high-
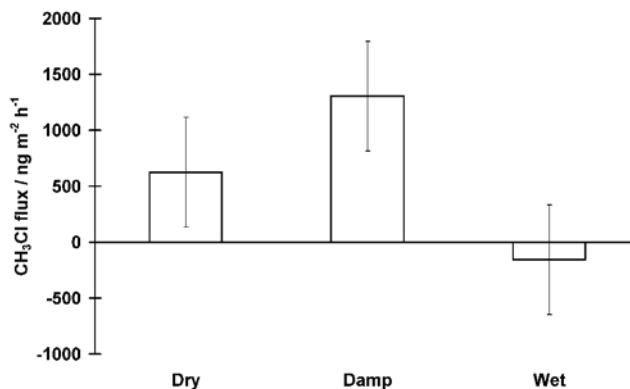

Figure 3. Average CH_3Cl fluxes during the seasonal study as a function of location hydrological classification. Error bars illustrate the magnitude of the limit of detection (± 490 ng m^{-2} h^{-1}) for an individual net CH_3Cl flux measurement.

latitude wetlands in Ireland [*Dimmer et al.*, 2001] and Scotland (C. J. Hardacre, unpublished, 2009).

5. Global Implications

[24] *Rhew et al.* [2007] estimated net annual uptake rates of 0.3 Gg CH_3Br and 11.2 Gg CH_3Cl for tundra worldwide assuming a total tundra surface area of 7.3×10^{12} m^2 and that their average net fluxes of -18 ng CH_3Br m^{-2} h^{-1} and -637 ng CH_3Cl m^{-2} h^{-1} applied over a 100-day growing season to all such ecosystems globally. The CH_3Br flux data from this study suggest that this CH_3Br estimate does not need to be revised. However, the small net CH_3Cl emission observed in this work suggests that the previous extrapolated global net uptake estimate for CH_3Cl may need to be revised downward to take account of these data for the Swedish arctic.

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