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Long-term CH₃Br and CH₃Cl flux measurements in temperate salt marshes

Long-term CH_3Br and CH_3Cl flux measurements in temperate salt marshes

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Abstract

Fluxes of CH_3Br and CH_3Cl and their relationship with potential drivers such as sunlight, temperature and soil moisture, were monitored at fortnightly to monthly intervals for more than two years at two contrasting temperate salt marsh sites in Scotland. Manipulation experiments were conducted to further investigate possible links between drivers and fluxes. Mean (± 1 sd) annually and diurnally-weighted net emissions from the two sites were found to be 300 ± 44 ng m^{-2} h^{-1} for CH_3Br and 662 ± 266 ng m^{-2} h^{-1} for CH_3Cl. A tentative scale-up indicates that salt marshes account for 0.5–3.2% and 0.05–0.33%, respectively, of currently-estimated total global production of these two gases, in line with previous findings from this and other research groups, but consistently lower than past global scale-up estimates from Southern Californian salt marshes. Fluxes followed both seasonal and diurnal trends with highest fluxes during summer days and lowest (negative) fluxes during winter nights. Statistical analysis generally did not demonstrate a strong link between temperature or sunlight levels and methyl halide fluxes, although it is likely that temperatures have a weak direct influence on emissions, and both certainly have indirect influence via the annual and daily cycles of the vegetation. CH_3Cl flux magnitudes from different measurement locations depended on the plant species enclosed whereas such dependency was not discernible for CH_3Br fluxes. In 14 out of 19 collars CH_3Br and CH_3Cl net fluxes were significantly correlated. The CH_3Cl/CH_3Br net-emission mass ratio was 2.2, a magnitude lower than mass ratios of global methyl halide budgets (~22) or emissions from tropical rainforests (~60). This is likely due to preference for CH_3Br production by the relatively high bromine content in the salt marsh plant material.

1 Introduction

The methyl halides CH_3Br and CH_3Cl are the most abundant natural vectors of bromine and chlorine into the stratosphere and consequently play an important role

in stratospheric ozone destruction. The current knowledge of their respective natural sources is incomplete leading to large uncertainties in their global budgets. Besides the issue of quantification, characterisation of possible sources is needed to assist modelling the impacts of future land-use and climate change on the stratosphere.

During the last decade a number of studies of CH_3Br and CH_3Cl fluxes at salt marshes have been conducted in Europe, Australia, the US and China with widely differing findings in regard to magnitude and drivers. Whilst extrapolation of flux measurements conducted in Southern California (Rhew et al., 2000, 2002; Manley et al., 2006) indicated that salt marshes could be responsible for 7–12% and 4–5% of global CH_3Br and CH_3Cl production, respectively, measurements in Tasmania by Cox et al. (2004), in Ireland by Dimmer et al. (2001) and in Scotland by Drewer et al. (2006) suggest that salt marshes are likely to account for less than 2% of global CH_3Br and no more than 0.03% of global CH_3Cl production (all estimates based on a global salt marsh area of $0.38 \times 10^{12} \, m^2$, Woodwell et al., 1973). The study by Wang et al. (2006) identified a Chinese salt marsh as a net sink of CH_3Cl. All groups except Wang et al. (2006) identified plants as a strong source of methyl halides whilst sediments were identified as weak emitters or sinks. The different groups found either sunlight, temperature, season or different plant growth stages as the most likely drivers of temporal methyl halide flux variations, with Rhew et al. (2000) and Manley et al. (2006) identifying plant species as the cause of spatial flux variation. Of the other studies, only Drewer et al. (2006) attempted to identify factors underlying the spatial variation and suggested sediment bromide content as a possible contributor. In general, fluxes of CH_3Br and CH_3Cl were found to be positively correlated with each other.

In summary, there are currently no conclusive data on both the size and drivers of methyl halide emissions from salt marshes. Furthermore many of the above studies comprised only a limited number of individual measurements often missing possible annual and/or diurnal flux variations. Thus gaps remain in the knowledge of both quantification and characterisation which must be filled in order to gain a clearer picture of the current and future impact of salt marshes on atmospheric chemistry. The aim of

this study was to expand a previous monitoring project for CH_3Br fluxes at a Scottish salt marsh to include a second site and measurement of CH_3Cl as well. Measurements were conducted for more than 2 yr at Heckie's Hole and Hollands Farm salt marshes on the east and west coasts of Scotland, respectively, comprising more than 450 individual daytime measurements in all seasons and more than 100 diurnal measurements.

2 Site descriptions

Heckie's Hole salt marsh (56°1′ N 2°35′ W), located in East Lothian at the mouth of the River Tyne flowing into the North Sea (Fig. 1), is surrounded on three sides by (wooded) dry land and protected from direct wave action. The site is characterised by very gentle inclines (<0.04%) dissected by deep tidal creeks. Vegetation cover is dense and dominated by *Puccinellia maritima* in the lower parts and an *Armeria maritima-Puccinellia maritima* vegetation mixture in the upper marsh but without strong zonation. Other, minor, species found at this salt marsh are *Aster tripolium*, *Glaux maritima*, *Salicornia europea*, *Spergularia media* and *Suaeda maritima* as well as *Plantago maritima* and *Triglochin maritima* which often occur as dense, mono-specific stands. Sediments at Heckie's Hole were characterised as silty loam with organic matter content in the range 10.3–22.3%.

Hollands Farm salt marsh (54°58′ N 3°29′ W) is situated besides the estuary of the River Nith as it flows into the Solway Firth on the west coast of the British mainland (Fig. 1). The marsh is open to the sea and subject to constant tidal wave action, and has accumulated appreciable amounts of sediment over the last few years. The landscape is characterised by a gently inclining lower marsh (~0.13%), inland of which a small upper marsh area rises via two small steps of ~20 cm and ~40 cm. The lower marsh contains at least three distinct topographical and vegetation zones starting from the sea with a flat, sparsely vegetated zone mainly comprising *Puccinellia maritima*, intermittent areas of hollows and hummocks covered by *Aster tripolium*, and a narrow zone nearest to the mainland which is covered by a mix of *Aster tripolium*, *Juncus*

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gerardi, *Plantago maritima*, *Puccinellia maritima* and *Triglochin maritima* and which is markedly wetter than the other parts of the lower marsh. The upper marsh is covered by a mixture of mainly graminoid species including *Carex binerva*, *Festuca rubra*, *Juncus gerardi*, *Puccinellia maritima* and *Triglochin maritima*. Minor species that occur
5   sparsely at the site are *Armeria maritima*, *Glaux maritima* and *Trifolium repens*. Sediments at Hollands Farm were characterised as sandy loam with organic matter content in the range 1.8–4.4%.

The climate at both sites is classified as *Cfb* in the Köppen-Geiger climate classification, being temperate maritime, wet all year round with long cool summers (Peel et al.,
10   2007).

3   Methods

3.1   Field enclosures

The main body of the work at the two salt marshes was the regular measurement of fluxes at the same sampling points throughout the whole year. At each sampling point
15   a collar constructed of 10–20 cm high, 40 cm internal diameter opaque PVC pipe with a fitting flange of outer diameter 50 cm of the same material was permanently inserted into the ground. The collars were inserted flush to the ground to reduce any impact of the collar rims on the enclosed space.

At Heckie's Hole two pairs of collars were installed in each of the lower (collar pairs
20   A and B) and upper salt marsh areas (collar pairs C and D) on the 26 May 2007. All collars were situated within the eulittoral (intertidal) zone, i.e. between the spring high tide line and the neap low tide line, with a range of vertical elevation across all collars of only 14 cm. All collars at this site were therefore subject to regular inundation.

At Hollands Farm a single collar was installed on a bare patch of sediment (collar
25   E) in the lower marsh area and one collar pair each on the previously described flat area (collar pair G), on the hummocks (collar pair F) and the wet area nearest to the

mainland (collar pair H) on the 30 and 31 May 2007. In the upper marsh one collar pair (I) was installed at the same time, and a second collar pair (J) on the 8 May 2008. At Hollands Farm the range in vertical elevation across all collars spanned 106 cm; all collars designated "lower" (collar E and collar pairs F–H) were situated in the eulittoral zone with regular inundation, whereas collars designated "upper" (collar pairs I+J) were in the supralittoral zone with only occasional inundation.

At both salt marshes the two collars of a collar pair were placed no more than 5 m apart, representing the typical vegetation of a particular part of a salt marsh but were not intended as replicates. In nearly all cases collars contained mixtures of species, as described also in Table 1. Halfway between each collar pair a 50 cm depth dip well was installed to measure water table depth. Flux measurements were conducted at fortnightly to monthly intervals between 4 June 2007 to 20 July 2009 at Heckie's Hole and 6 June 2007 to 21 July 2009 at Hollands Farm.

To start a flux measurement a cylindrical, 40 cm diameter chamber, made of 0.5–1.0 mm thick translucent polyethylene terephthalate (typical transmission in the PAR region ≈90%) and equipped with forced air circulation and a gas sampling port, was placed on top of the collar flange and clamped airtight with bulldog clips. The chambers were 21.5 cm high (except for the 6 June 2007 at Hollands Farm where 10.5 cm high chambers were also used). Typically, sampling for flux measurements took place between 10 a.m. and 3 p.m. (except for diurnal studies). At the end of the 10 min enclosure time a 550 mL air sample was extracted and stored in a 1 L Tedlar bag. Contemporaneous samples of ambient air were collected and stored similarly.

Concurrently with each enclosure, internal chamber temperature and PAR were recorded at 2 s intervals and a reading of ambient air temperature, soil temperature at 10 cm depth and water table depth in the dip well was taken. The mean internal chamber temperature during an enclosure was 5.8 °C above ambient air temperature. Soil samples (0–8 cm depth) for moisture determination were also taken on most measurement occasions from the immediate vicinity of the individual collars, stored in air-tight bags for transport to the laboratory and then refrigerated until analysis.

3.1.1 Diurnal flux measurements

To investigate the behaviour of methyl halide fluxes throughout the day diurnal measurement campaigns were conducted. Fluxes were measured for one collar of each collar pair (normally choosing the stronger emitting one) every 4.8 h 5 times at Hollands Farm and 6 times at Heckie's Hole. At Heckie's Hole the time of day of the first and last measurement cycle therefore coincided. Diurnal measurements were conducted three times at both locations, twice during summer and once during winter.

3.1.2 Shading experiment

On the 31 May 2009 a separate field experiment to study the influence of sunlight on methyl halide fluxes was carried out at Heckie's Hole. First, fluxes from each collar pair were measured in the usual way with the transparent 21.5 cm high chamber for 10 min. Then, for one collar of each pair, the measurement was repeated with the chamber and the PAR and temperature sensors beneath a 95 cm long × 62 cm wide × 47 cm high scaffold covered with a semi-transparent green netting. Finally, the scaffold was covered by a blanket and a third enclosure undertaken in total darkness. This was repeated for all four collar pairs at the salt marsh. The aim was to reduce the incident sunlight whilst maintaining the temperature inside the chamber as constant as possible, so as to distinguish between sunlight and air temperature as drivers for methyl halide fluxes. Due to problems with the analytical equipment at the time only CH_3Br fluxes were quantified.

3.1.3 Vegetation removal experiment

On the 16 and 18 June 2009 at Hollands Farm and Heckie's Hole, respectively, above-ground vegetation from all salt marsh collars was removed using scissors to determine the mass and make-up of the vegetation. In the laboratory it was sorted by species and dead plant material removed. The sorted plant material was then oven dried at 70 °C

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as described below. Methyl halide fluxes were measured immediately before (in most cases) and after vegetation removal and then on two more occasions at fortnightly intervals. Between measurements the collars were covered with a black landscaping textile to slow vegetation regrowth and any new vegetation was removed before undertaking subsequent measurements. Due to problems with the analytical equipment at the time only CH$_3$Br fluxes could be retrieved in the initial stages of this experiment.

3.1.4 Testing of flux linearity

An enclosure time of 10 min was chosen to ensure a large enough accumulation/depletion of methyl halides even from weakly emitting/uptaking collars for subsequent GC-analysis. However, it had to be ascertained if and by how much inferred fluxes differed over the enclosure duration. Thus on a few occasions fluxes were measured in short succession from individual collars at increasing enclosure durations, ranging from 2.5 to 40 min. Although the outcome was not entirely conclusive, results suggest that CH$_3$Br and CH$_3$Cl fluxes extrapolated to an ideal "0" min enclosure time could be on average a factor of 1.5 times the fluxes derived after 10 min enclosure. Although these findings are not used in the reporting of the measured fluxes, they are considered as potential uncertainties in the subsequent tentative scale-up.

3.2 GC analysis

Briefly, 100 mL aliquots of each sample were analysed using an HP5890 GC-ECD with a custom-built two-stage cryogenic pre-concentration unit (Hardacre et al., 2009). The first stage comprised an absorbent trap filled with Tenax TA 60/80 (Supelco, Bellefont, PA, USA), cooled with two-stage Peltier cells to −28 °C. The second stage was a cryogenic trap filled with glass beads and cooled with dry ice to −78 °C. Separation was carried out with a ZB624 column (Phenomenex Inc., Torrence, CA, USA), length 30 m, i.d. 0.32 mm, and a temperature programme of 5 min at 40 °C, ramp to 240 °C over 5 min and hold for another 5 min. Five-point calibrations were undertaken using

dilutions into zero air from certified CH_3Br standard (500 ± 10 ppbV in N_2, Air Products Inc., Allentown, PA, USA), and CH_3Cl standard (15.80 ± 0.47 ppmV in N_2, Air Liquide, Paris, France). Accuracy and precision uncertainty combined was quantified as $\pm 15\%$ for both gases at mixing ratios around ambient.

Enclosure net fluxes were derived from the difference between sample and ambient background values and expressed per m^2 per h. The uncertainties in flux values quoted here combine the uncertainties in both instrumental determination of methyl halide concentration in a gas sample and in the enclosure parameters used to convert mixing ratios to fluxes. The main sources of uncertainty derive from interpolation of the calibration curve. Blank and storage experiments were conducted and found not to contribute uncertainty greater than the general magnitude of the other uncertainties present and quantified. Since both the background air and enclosure samples were stored in identical conditions such uncertainties are minimised by the experimental procedure of quantification by difference.

Discrimination of a significant net flux depends on the ability to determine significant difference in analyte mixing ratio between an enclosure sample and parallel background air sample. The LOD for determination of a net flux was thus set at twice the uncertainty in the associated background sample. The LOD values vary between individual flux measurements because the uncertainty in the background measurement varies with the calibration curve used for that pair of sample and background determinations. The interquartile ranges of individual sample LOD values were 34–71 and 340–750 ng m^{-2} h^{-1} for CH_3Br and CH_3Cl fluxes, respectively, with lower sample values having lower associated LOD values (because of better linear calibrations over smaller concentration ranges). Where a flux measurement was below its estimated LOD the flux was set to zero for all futher data processing. Before January 2008 the ECD had not yet been converted to oxygen doping and therefore only CH_3Br measurements are available prior to then.

3.3 Determination of soil and plant dry mass

Soil and plant samples were oven dried at 105 °C and 70 °C, respectively, to constant mass. For soils, gravimetric water content was determined by weighing before and after oven drying.

3.4 Bromine and chlorine content of plant material

Plant materials were analysed for both total chlorine and total bromine content using a custom-built XRF instrument. The analysis of the samples was carried out at the University of Heidelberg by Dr. Andriy K. Cheburkin.

Vegetation from each species was randomly sampled from both salt marshes (except *Salicornia europea* which was collected only at Heckie's Hole) and the sub-samples mixed into a single sample per species. The fresh material was washed with de-ionised water and then dried in an oven at 70 °C to constant mass. Once dried, the samples were stored in air-tight bags and shipped to Germany for analysis.

Combined total chlorine and bromine analysis was carried out on the TITAN-XRF (Cheburkin and Shotyk, 2005), an energy-dispersive XRF spectrometer specifically built for analysis of peat and plant samples. Calibration was carried out with certified plant materials with known halogen content and analytical uncertainty was estimated to be less than 10%.

4 Results and discussion

4.1 Methyl halide flux quantification summary

The mean, minimum and maximum daytime methyl halide fluxes measured for the collars at both salt marsh sites together with data on collar vegetation are displayed in Table 1. Mean CH_3Br fluxes at Heckie's Hole (Table 1a) were in general larger than fluxes recorded at Hollands Farm (Table 1b). Moreover there was a marked zonation

of mean CH$_3$Br fluxes at Hollands Farm, with fluxes at the lower marsh collars (pairs F–H) being up to 4 times greater than at the upper marsh collars (pairs I and J). CH$_3$Br fluxes at Hollands Farm also tended to be more extreme with flux maxima being much larger than those at Heckie's Hole. No CH$_3$Br net uptake was recorded in either salt
5 marsh site during the 26 months of measurements.

Mean CH$_3$Cl fluxes at both salt marsh sites were higher than CH$_3$Br fluxes and were negative (net uptake) on some occasions. CH$_3$Cl flux magnitudes from collars at Heckie's Hole were positively correlated with the total dry mass of *Puccinellia maritima* present ($R=0.94$, $P=0.0004$). For this reason mean CH$_3$Cl fluxes were less ho-
10 mogeneous than CH$_3$Br fluxes and mean fluxes from the lower marsh collars dominated by *Puccinellia maritima* (A2, B1 and B2) were up to 3 times as high as fluxes from the upper marsh area which has a larger proportion of *Armeria maritima*. For the same reason CH$_3$Cl fluxes from collar A1 were considerably lower than for the rest of the lower marsh as it was dominated by *Plantago maritima*. In contrast, at
15 Hollands Farm, mean flux magnitudes were negatively correlated with dry mass of *Puccinellia maritima* ($R=-0.87$, $P=0.001$) but positively correlated with dry mass of *Aster tripolium* ($R=0.85$, $P=0.002$), *Juncus gerardi* ($R=0.65$, $P=0.04$) and *Plantago maritima* ($R=0.84$, $P=0.003$) resulting in a much stronger zonation of flux magnitudes at Hollands Farm. This finding can be partially explained by the fact that the vegetation
20 mixture and abundance of plant species differs between the two salt marsh sites. No such correlation between vegetation and flux magnitudes was found for CH$_3$Br.

For 14 out of the 19 collars across both salt marshes there was a statistically significant ($P<0.05$) positive correlation between CH$_3$Br and CH$_3$Cl fluxes, in line with previous findings by Cox et al. (2004), Rhew et al. (2000) and Manley et al. (2006).
25 Mean CH$_3$Cl/CH$_3$Br mass flux ratio was 2.2.

4.2 Annual and diurnal flux variations

In Fig. 2, annual and diurnal fluxes from an example collar, D2 at Heckie's Hole, are presented together with air temperature and PAR values at the time of enclosure. Also shown in Fig. 2a is the growing season as a grey shade from the beginning of April to the end of October (days 91–304). The growing season was taken as the period between the appearance of the first green shoots in spring to the dying off of all vegetation in autumn.

As shown in Fig. 2a CH_3Br fluxes follow an annual cycle with highest fluxes during the growing season and lowest or no fluxes during the non-growing season. An interesting observation was that fluxes from the different collars at Heckie's Hole followed similar patterns to each other in a given year, i.e. had some spatial homogeneity, but patterns differed between the three calendar years and peaked at different times. This indicates that there is indeed a common factor driving annual emissions from salt marshes. However, at Hollands Farm, the patterns of methyl halide fluxes from individual collars in the different years varied more between the different collar pairs than between the two collars of a collar pair indicating that either ground conditions or vegetation make-up are also important in the response of methyl halide fluxes to climatic drivers. From studies with stands of mono-specific flowering plants it has been suggested that peaks in methyl halide emission may be associated with flowering events (Manley et al., 2006) but with the mixed-species enclosures in this work such a direct association was not discernible. Non-growing season daytime net emissions of CH_3Br were on average 22% of growing season emissions at Heckie's Hole and 34% at Hollands Farm. The corresponding figures for CH_3Cl are 13% and 16% at Heckie's Hole and Hollands Farm, respectively.

Methyl halide fluxes during the growing season consistently showed a diurnal pattern with highest fluxes during daylight hours and lowest fluxes during night time (Fig. 2b). However, CH_3Br nighttime fluxes typically did not cease but dropped on average to 70% of daytime fluxes at Heckie's Hole and 60% of daytime fluxes at Hollands Farm

whilst CH_3Cl fluxes often dropped to zero or were negative at some point during the night (average daytime/nighttime flux ratio 40% at Heckie's Hole and 60% at Hollands Farm). During the non-growing season CH_3Br fluxes followed a much weaker diurnal cycle with a similar pattern whilst CH_3Cl fluxes often appeared to be random. There is currently no suggested reason for this differing behaviour.

4.3 Statistical analysis of potential flux drivers

The correlations of potential drivers such as air temperature, soil temperature, internal chamber temperature during enclosure, PAR levels, depth of water table and soil moisture with methyl halide fluxes from individual collars were examined. To distinguish better between the influence of potential drivers on the vegetation, which measurements suggested was the main source of methyl halides, and the sediment as a minor source or sink, the linear correlation between drivers and methyl halide fluxes was tested separately for fluxes during growing and non-growing seasons. Only correlations significant at $P<0.05$ are discussed here.

As shown in Fig. 2a CH_3Br fluxes roughly followed the trend of air temperatures whilst CH_3Cl fluxes, if they showed any dependency at all, follow PAR levels; statistical analysis suggests that both methyl halide fluxes, particularly during the growing season, depended more strongly on temperatures. Growing season CH_3Br fluxes at Heckie's Hole were in 7 out of 8 collars significantly correlated with internal chamber temperature ($0.46 \leq R \leq 0.63$), in 6 collars with ambient air temperature ($0.47 \leq R \leq 0.73$) and in 5 collars with soil temperature ($0.49 \leq R \leq 0.80$), whereas there was no significant correlation with PAR for any collar. At Hollands Farm the correlations between temperatures and growing season CH_3Br fluxes were weaker, with fluxes in 5 out of 11 collars being correlated with internal chamber temperature and 4 collars showing correlation with ambient air temperatures, whilst there was a significant negative correlation with soil temperatures at two collars. Again no correlations between CH_3Br fluxes and PAR levels were found. CH_3Cl fluxes during the growing season at both salt marsh sites seemed less correlated with any of the monitored factors, with only

4 significant positive correlations with temperatures at Heckie's Hole and two negative correlations with temperatures at Hollands Farm.

At Heckie's Hole non-growing season CH$_3$Br fluxes from all collars were significantly and often strongly positively correlated with ambient air, soil and internal chamber temperatures, whilst fluxes from only 3 collars were significantly correlated with PAR levels. In contrast, non-growing season CH$_3$Cl fluxes at Heckie's Hole were positively correlated with PAR levels in 6 collars but at only one collar were fluxes correlated with ambient air and soil temperatures and at only 3 collars with internal chamber temperatures. At Hollands Farm non-growing season CH$_3$Br fluxes were positively correlated with PAR in 4 out of 11 collars and with soil temperature, ambient air temperature and internal chamber temperature for 1, 3 and 4 collars, respectively. At the same time CH$_3$Cl fluxes from 2 collars were positively correlated with PAR, and from one collar each with either of the three different temperature measures.

Fluxes were correlated with either soil moisture or water table depths for only 6 collars across both salt marshes, being either negative or positive. It therefore appears that these factors do not directly influence instantaneous methyl halide fluxes in a significant manner, although soil moisture conditions generally will certainly influence the plant species prevalent in different zones of a salt marsh.

In summary, variations in fluxes of methyl halides, especially of CH$_3$Br, during the growing season, when most of the methyl halides are produced, seem generally associated with changes in temperature. However, the influence of measures of temperature or sunlight was only assessed for their direct effect on methyl halide fluxes and did not take into account indirect influences of temperature or sunlight on vegetation growth or metabolism beyond the rather crude measure of growing and non-growing season.

4.4 Shading experiment

PAR levels during the shading experiment decreased on average from ~1430 μmol m^{-2} s^{-1} without shade to ~450 μmol m^{-2} s^{-1} under the netting to 0 μmol m^{-2} s^{-1} under

the blanket, whilst internal chamber temperatures changed from 28.6 °C to 25.8 °C and then to 22.2 °C, respectively. CH$_3$Br fluxes during the shading experiment did not change significantly between the different treatments (at $P < 0.05$) therefore strongly suggesting that PAR does not directly influence CH$_3$Br emissions from vegetation within the ~20 min time-scale of the treatment.

4.5 Vegetation removal experiment

CH$_3$Br fluxes measured a few minutes after complete vegetation removal were for all collars significantly lower than the corresponding fluxes measured both directly before removal on the same day or most recently prior to that ($P=0.001$ at Heckie's Hole and $P=0.003$ at Hollands Farm). However, as with the diurnal studies, CH$_3$Br fluxes did not generally fall to zero but stayed at a low level. These emissions then decreased on the following two fortnightly measurement occasions. At Hollands Farm CH$_3$Br fluxes after vegetation removal were compared in a two-tailed t-test against all seasonal CH$_3$Br measurements from collar E, which did not contain any vegetation, and no significant differences in flux magnitudes were found. This indicates that emissions/uptake of CH$_3$Br from collar E is representative of fluxes of sediment for the whole of Hollands Farm.

As noted above, CH$_3$Cl measurements were not available at the time of vegetation removal itself but on the two occasions two and four weeks after vegetation removal. After vegetation removal CH$_3$Cl fluxes at both salt marshes dropped to values near or below the LOD. At Hollands Farm CH$_3$Cl uptake at some collars was recorded. One-tailed t-tests showed that CH$_3$Cl fluxes for both salt marshes were significantly lower after plant removal ($P=0.0001$ for Heckie's Hole and $P=0.001$ for Hollands Farm) and, similarly to CH$_3$Br, CH$_3$Cl fluxes at Hollands Farm after plant removal were found to be not significantly different from fluxes from collar E.

In summary there is, as expected from earlier reports, strong evidence that both CH$_3$Cl and CH$_3$Br are primarily produced by vegetation rather than by micro-organisms in the soil. The findings from this experiment also indicate that below-ground plant

biomass, such as roots and rhizomes, is either not involved or plays only a minor part in methyl halide production.

4.6 Total bromine and chlorine content

The total bromine and chlorine concentrations measured in the above-ground vegetation collected at Heckie's Hole and Hollands Farm (Table 2), together with the data on vegetation composition and mass for each collar, were used to estimate the average halogen concentration and total halogen content of the vegetation enclosed in each collar at both salt marsh sites. This was done by multiplying the dry mass of each species by the XRF-derived halogen concentration for the respective species and subsequent summation for all species in an individual collar. For *Triglochin maritima* the chlorine concentration was estimated from the bromine concentration and the orthogonal distance regression fit of all other available bromine and chlorine concentration pairs. Halogen concentrations for *Festuca rubra* were taken as the mean values from the other graminoid species *Carex binerva*, *Juncus gerardi* and *Puccinellia maritima* for which data were available. Comparing these calculated halogen content values with the mean methyl halide flux magnitudes from the collars did not reveal any statistically significant correlations. This indicates that variations in halogen content/concentration typically found in salt marsh vegetation do not explain spatial differences in methyl halide fluxes. Indeed, the amounts of bromine and chlorine released from plants via methyl halide emissions are only a small fraction of the total halogen pool available so conversion of halogens into methyl halides is likely to be the limiting factor. This makes it more likely that biological processes associated with plant species themselves are the determining factor in methyl halide flux magnitudes as argued by Manley (2002). As shown in Table 2 the Cl/Br mass ratio in the different plant species varied between 96 to 245 whereas the mean Cl/Br mass ratio in methyl halide emissions was only 1.8 (calculated from the observed CH$_3$Cl/CH$_3$Br mean net-emission mass ratio of 2.2). There is therefore a clear preference for CH$_3$Br production over CH$_3$Cl production, or

the corollary of suppression of CH_3Cl production due to competitition by the more nucleophilic Br^- ions.

4.7 Interpolation and upscaling

In order to assess the potential global implication of findings from this work a tentative global estimate from the measured fluxes was derived in 8 steps.

1. Seasonal flux data from the 3 calendar years of measurements for a given collar were merged into one hypothetical year with 365 Julian days. For each day methyl halide fluxes for every collar were derived – if not already available from measurements – by linear interpolation between recorded flux data for that collar, resulting in 365 flux values for CH_3Br and CH_3Cl for each collar.

2. For each salt marsh, a mean methyl halide flux value, representing the entire salt marsh area, was derived for each day j by spatially-weighted averaging of fluxes from individual collars i at that salt marsh. Spatial weighting was based on the proportion of a vegetation zone relative to the total salt marsh area. The formula was

$$F_{j,\text{sa}} = \sum_i \left(F_{ij} \times A_i \right)$$

where $F_{j,\text{sa}}$ is the spatially weighted mean methyl halide flux for the whole salt marsh on day j and F_{ij} is the methyl halide flux for each individual collar derived from interpolation of the seasonal flux data. A_i is either the relative proportion of a vegetation zone represented by a collar or, if a vegetation zone is represented by n collars, the n-th part of the relative proportion of a vegetation zone of the total salt marsh area ($0 \leq A_i \leq 1$, $\sum A_i = 1$).

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3. For both sites the number of hours of daylight and darkness for each Julian day were calculated using the formula

$$\cos\chi = \cos(\text{LHA}) \times \cos(\text{LAT}) \times \cos(\text{DEC}) + \sin(\text{LAT}) \times \sin(\text{DEC})$$

where $\angle\chi$ is the solar zenith angle at a given time and location, $\angle\text{LAT}$ is the latitude of the measurement site, $\angle\text{DEC}$ is the declination of the Earth to its orbital plane on that Julian day and $\angle\text{LHA}$ is a measure of the time within that day. By setting $\cos(\chi)$ to 1 and solving for $\angle\text{LHA}$ the length of the day as the time between sunrise and sunset was derived.

4. For each site the average ratio of nighttime to daytime methyl halide fluxes ($r_{n/d}$) was calculated separately for the growing and non-growing season.

5. For each Julian day the daily flux ($\text{ng m}^{-2}\,\text{d}^{-1}$) was calculated from the interpolated, spatially averaged hourly fluxes, the length of daytime and nighttime hours and the ratio of nighttime/daytime fluxes (Fig. 3). The total annual flux ($\text{ng m}^{-2}\,\text{yr}^{-1}$) for each salt marsh was calculated by summing over all days as shown below.

$$F_{\text{tot}} = \sum_{j=1}^{365} \left(\left(t_{j,\text{dt}} \times F_{j,\text{sa}}\right) + \left(t_{j,\text{nt}} \times F_{j,\text{sa}} \times r_{j,n/d}\right)\right)$$

Here F_{tot} is the total annual methyl halide flux, and $t_{i,\text{daytime}}$ and $t_{i,\text{nighttime}}$ are the number of hours between sunrise and sunset or between sunset and sunrise, respectively, for each Julian day.

6. For better comparability with flux measurements from other groups F_{tot} was divided by 365 days per year and 24 h per day to return to a mean hourly flux for each salt marsh ($\text{ng m}^{-2}\,\text{h}^{-1}$), but now weighted according to the seasonal and daily variations in flux and the distribution of vegetation at that salt marsh.

7. Standard deviation values for the final weighted mean hourly flux at each salt marsh were derived by multiplying these values by the average relative standard deviations of the daytime fluxes at that salt marsh.

8. To obtain a value for global annual salt marsh fluxes, the mean of the two final weighted methyl halide fluxes from Heckie's Hole and Hollands Farm were multiplied by estimates of global salt marsh area (see below). For the resulting global estimates no standard deviation values are given since it is felt that they would imply an unrealistic level of precision.

The resulting spatially, seasonally and daily weighted mean (± 1 sd) hourly fluxes at each salt marsh were $335 \pm 45 \, \text{ng m}^{-2} \, \text{h}^{-1}$ for CH_3Br and $733 \pm 280 \, \text{ng m}^{-2} \, \text{h}^{-1}$ for CH_3Cl at Heckie's Hole and $264 \pm 44 \, \text{ng m}^{-2} \, \text{h}^{-1}$ for CH_3Br and $591 \pm 253 \, \text{ng m}^{-2} \, \text{h}^{-1}$ for CH_3Cl at Hollands Farm. The CH_3Br flux values at Heckie's Hole are therefore in excellent agreement with the findings of Drewer et al. (2006) who measured CH_3Br at the same site and reported mean emissions of $350 \, \text{ng m}^{-2} \, \text{h}^{-1}$ (without taking into account diurnal variation in emissions).

Taking the mean values from the two sites as $300 \pm 44 \, \text{ng m}^{-2} \, \text{h}^{-1}$ for CH_3Br and $662 \pm 266 \, \text{ng m}^{-2} \, \text{h}^{-1}$ for CH_3Cl and scaling up by the total global salt marsh area estimates of $0.38 \times 10^{12} \, \text{m}^2$ from Woodwell et al. (1973) and $1.65 \times 10^{12} \, \text{m}^2$ from Costanza et al. (1997) yields global estimates of 1.0 and $4.3 \, \text{Gg yr}^{-1}$ for CH_3Br and 2.2 and $9.6 \, \text{Gg yr}^{-1}$ for CH_3Cl. These values would rise if taking into account the previously-mentioned possible non-linearity of measured fluxes with enclosure time, increasing the upper range values to $6.5 \, \text{Gg yr}^{-1}$ and $14.3 \, \text{Gg yr}^{-1}$ for CH_3Br and CH_3Cl, respectively. These ranges of values are equivalent to 0.5–3.2% and 0.05–0.33% of the global annual CH_3Br and CH_3Cl budgets, respectively, given in the most recent WMO report (Clerbaux et al., 2007). The results from this study are in line with the mean flux values reported by Dimmer et al. ($320 \, \text{ng m}^{-2} \, \text{h}^{-1}$ CH_3Br, $380 \, \text{ng m}^{-2} \, \text{h}^{-1}$ CH_3Cl), Cox et al. ($190 \, \text{ng m}^{-2} \, \text{h}^{-1}$ CH_3Br, $300 \, \text{ng m}^{-2} \, \text{h}^{-1}$ CH_3Cl) and Drewer et al. ($350 \, \text{ng m}^{-2} \, \text{h}^{-1}$ CH_3Br) for temperate salt marshes but are up to two orders of magnitude smaller than

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mean fluxes reported for Mediterranean climate salt marshes in Southern California by Rhew et al. (4210 ng m^{-2} h^{-1} CH$_3$Br, 51 100 ng m^{-2} h^{-1} CH$_3$Cl) and Manley et al. (7 300 ng m^{-2} h^{-1} CH$_3$Br, 46 800 ng m^{-2} h^{-1} CH$_3$Cl, vegetated areas only). This study therefore confirms again the very distinct flux magnitudes of methyl halides from salt

5 marshes in these two climates, highlighting the pitfalls of large-scale spatial extrapolation from a single example of an ecosystem when limited data are available.

The mean CH$_3$Cl/CH$_3$Br mass flux ratio of 2.2 observed in this study lies between the values of 1.2, 1.6, 12 and 6.4 calculated for other salt marshes from the data of Dimmer et al. (2001), Cox et al. (2004), Rhew et al. (2000) and Manley et al. (2006),

10 respectively, with the lower values being associated with the more temperate climate salt marshes. Interestingly, the ratio 2.2 is considerably lower than the ∼60 ratio in fluxes from vegetation in a tropical rainforest (Blei et al., 2010), or the ∼22 ratio in global CH$_3$Cl and CH$_3$Br budgets. The difference is most likely due to a suppression of CH$_3$Cl production by the more nucleophilic bromine/bromide when the concentration of

15 bromine in the plant material is relatively high, as for salt marsh vegetation. This further supports the finding that salt marshes are relatively more important for global CH$_3$Br budgets than for global CH$_3$Cl budgets, although again temperate and Mediterranean salt marshes appear to behave somewhat differently.

5 Conclusions

20 Positive net fluxes of CH$_3$Br and CH$_3$Cl at temperate salt marshes are principally associated with the vegetation. Temporal flux variations are clearly linked to both seasonal and diurnal cycles but no strong direct link of instantaneous flux to either temperature or sunlight levels was found. Spatial CH$_3$Cl flux variations were associated with the abundances of different plant species, although this was not discernible for CH$_3$Br.

25 Emissions of CH$_3$Br are greater relative to CH$_3$Cl from temperate salt marshes than from other sources. However, temperate salt marshes are unlikely to be a large global source of either methyl halide, amounting to only a few percent of total global annual

CH$_3$Br production and an order of magnitude less for CH$_3$Cl. In the light of these findings it is unlikely that future climate change would significantly alter the contribution of temperate salt marshes to global methyl halide budgets.

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Table 1. Summary of methyl halide fluxes and vegetation composition of collars at Heckie's Hole and Hollands Farm salt marsh sites. Shown are the mean, minimum and maximum fluxes and number (n) of daytime flux measurements, as well as the Pearson product-moment coefficient (R) between CH$_3$Br and CH$_3$Cl fluxes, the latter printed in bold where statistically significant at $P<0.05$. Vegetation composition is characterised by the total dry mass (m) of aboveground vegetation present in each collar at the end point together with the weight% of the two main species in each collar relative to the total vegetation composition. Species abbreviations are *Arm(eria maritima)*, *Ast(er tripolium)*, *Junc(us gerardi)*, *Car(ex binerva)*, *Fest(uca rubra)*, *Plan(tago maritima)*, *Pucci(nellia maritima)*, *Suae(da maritima)* and *Trig(lochin maritima)*. The last two columns give the total bromine and chlorine content of the aboveground vegetation calculated from species-specific halogen content and dry mass in each collar. All collars at Heckie's Hole were situated within the eulittoral (intertidal) zone. At Hollands Farm, all collars designated "lower" (collar E and collar pairs F–H) were situated in the eulittoral zone, whereas collars designated "upper" (collar pairs I+J) were in the supralittoral zone. (Futher details in the main text.)

	(a) Heckie's Hole															
	CH$_3$Br (ng m^{-2} h^{-1})				CH$_3$Cl (ng m^{-2} h^{-1})						vegetation composition					
Collar	Mean	Min	Max	n	Mean	Min	Max	n	R	m (g)	#1	(%)	#2	(%)	Br (mg)	Cl (mg)
A1	274	0	745	25	483	−499	2640	14	**0.86**	162	*Plan.*	(90)	*Pucci.*	(9)	69.8	12 300
A2	517	0	1110	30	1520	−201	6400	16	**0.88**	69	*Pucci.*	(98)	*Suae.*	(2)	6.0	918
B1	355	0	802	25	1480	0	5990	14	**0.87**	51	*Pucci.*	(100)	–		4.0	569
B2	337	0	717	30	1100	−145	5180	17	**0.83**	58	*Pucci.*	(94)	*Suae.*	(4)	6.1	999
C1	356	0	815	25	624	−1610	2960	13	**0.61**	62	*Arm.*	(50)	*Pucci.*	(36)	14.2	1660
C2	529	0	1100	31	585	−539	3540	18	**0.54**	52	*Pucci.*	(47)	*Arm.*	(38)	12.5	1390
D1	450	45	1140	25	383	−1270	1530	13	0.53	44	*Trig.*	(43)	*Plan.*	(33)	13.4	2020
D2	682	0	1610	30	950	−134	3820	17	**0.78**	69	*Pucci.*	(42)	*Arm.*	(39)	14.4	1730
all	445	0	1610	221	904	−1610	6400	122	**0.61**							

Table 1. Continued.

	CH$_3$Br (ng m^{-2} h^{-1})				CH$_3$Cl (ng m^{-2} h^{-1})						vegetation composition					
											(b) Hollands Farm					
Collar	Mean	Min	Max	n	Mean	Min	Max	n	R	m (g)	#1	(%)	#2	(%)	Br (mg)	Cl (mg)
E	20	0	139	26	78	−933	1510	15	0.16		– no vegetation –					
F1	858	122	3440	30	964	−344	3520	18	**0.80**	26	*Pucci.*	(84)	*Ast.*	(12)	2.8	444
F2	641	89	2850	25	684	−211	2700	14	**0.82**	22	*Pucci.*	(51)	*Fest.*	(45)	1.8	294
G1	214	0	521	24	521	0	2450	13	**0.73**	22	*Pucci.*	(100)		–	1.7	242
G2	408	0	1010	28	598	0	2870	16	**0.73**	20	*Pucci.*	(100)		–	1.5	222
H1	495	57	1990	27	4950	0	42 300	16	**0.28**	79	*Pucci.*	(77)	*Plan.*	(13)	12.5	2300
H2	522	0	2170	25	2540	0	9930	15	**0.77**	60	*Trig.*	(61)	*Plan.*	(17)	14.7	2180
I1	147	0	515	26	254	−2380	2220	15	**0.75**	47	*Junc.*	(48)	*Pucci.*	(34)	4.8	822
I2	197	0	753	23	108	−632	2300	13	0.24	35	*Pucci.*	(54)	*Junc.*	(38)	2.9	475
J1	181	0	560	12	952	−1780	5940	12	**0.91**	57	*Car.*	(62)	*Pucci.*	(32)	4.1	622
J2	133	0	418	14	2480	−1260	29 000	14	0.05	72	*Trig.*	(48)	*Fest.*	(36)	11.2	1520
all[a]	347	0	3440	234	1280	−2380	4230	146	**0.31**							

[a] except collar E, which did not contain any vegetation

Table 2. Bromine and chlorine concentrations measured by XRF in above-ground plant material from Heckie's Hole and Hollands Farm.

Species	Br (μg g^{-1})	Cl (mg g^{-1})	Cl/Br mass ratio
Armeria maritima	255	26.0	102
Aster tripolium	333	63.0	189
Carex binerva	55.3	9.30	168
Juncus gerardi	85.5	16.2	189
Plantago maritima	461	81.5	177
Puccinellia maritima	77.0	11.0	143
Salicornia europea	782	192	245
Spergularia media	912	87.4	96
Suaeda maritima	681	146	214
Triglochin maritima	213	n.a.	–

Fig. 1. Map of Scotland showing the approximate locations of the two salt marsh sites.
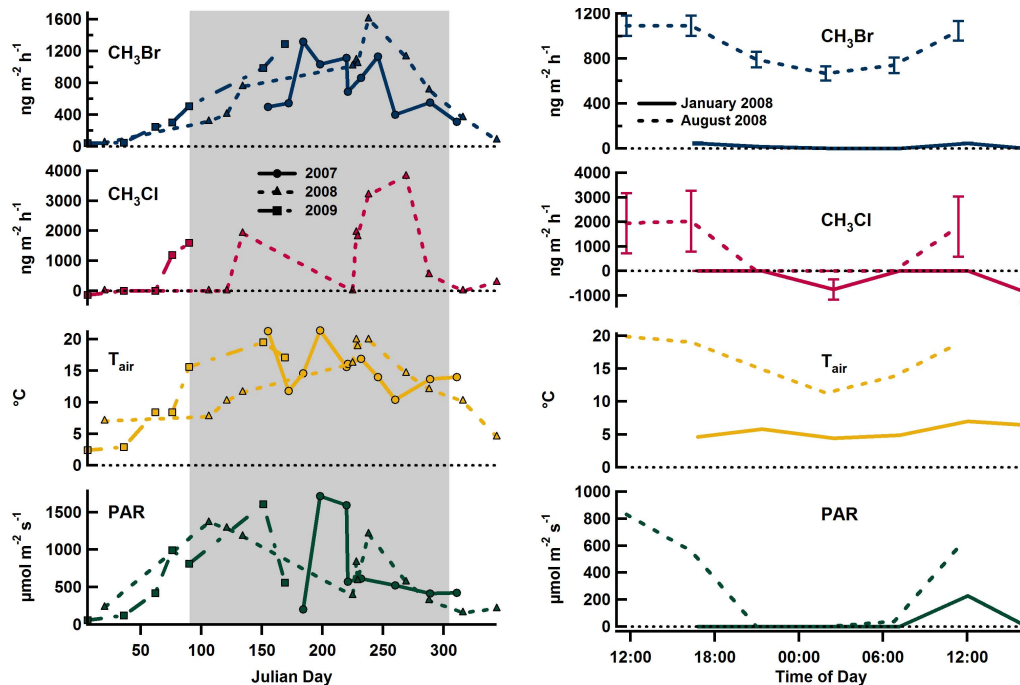
Fig. 2. Annual and diurnal methyl halide fluxes measured from collar D2 at Heckie's Hole salt marsh together with air temperature and PAR intensity at time of measurement. The shaded area in **(a)** demarcates the growing season. Annual fluxes are shown for all 3 calendar years and diurnal fluxes are shown for January 2008 and August 2008. Whiskers in **(b)** represent the standard deviation of flux values derived from combined sampling and analytical uncertainties.
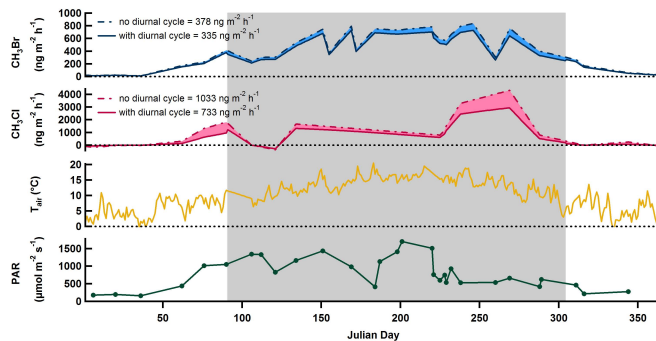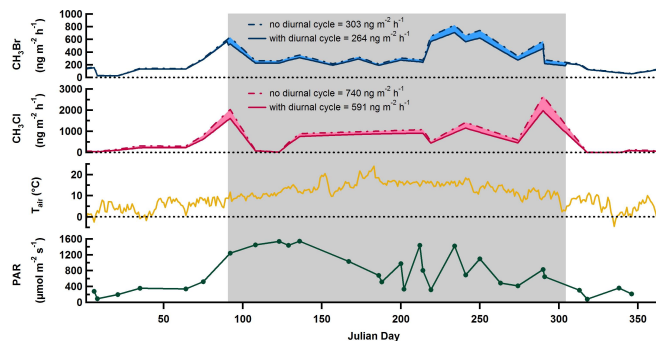
(a) Heckie's Hole

(b) Hollands Farm

Fig. 3. Interpolated measured hourly methyl halide fluxes (spatially weighted according to vegetation distribution) from Heckie's Hole and Hollands Farm together with PAR values at time of measurement and continuously-recorded air temperatures. Shaded areas indicate growing season. Methyl halide fluxes are shown with and without taking diurnal flux variations into account. Numbers given are the weighted mean annual flux values calculated as described in the text. T_{air} values are from a temperature data logger located at each salt marsh at 1.2–1.5 m height with 10 min logging intervals.

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