

Methyl bromide emissions to the atmosphere from temperate woodland ecosystems

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Abstract

The environmental importance of methyl bromide (CH₃Br) arises from its contribution to stratospheric ozone loss processes and, as a consequence, its emissions from anthropogenic sources are subject to the Montreal Protocol. A better understanding of the natural budget of CH₃Br is required for assessing the benefit of anthropogenic emission reductions and for understanding any potential effects of environmental change on global CH₃Br concentrations. Measurements of CH₃Br flux in temperate woodland ecosystems, in particular, are very sparse, yet these cover a large fraction of terrestrial land surface. Results presented here from 18 months of field measurements of CH₃Br fluxes in four static flux chambers in a woodland in Scotland and from enclosures of rotting wood and deciduous and coniferous leaf litter suggest net emissions from temperate woodlands. Net CH₃Br fluxes in the woodland varied between the chambers, fluctuating between net uptake and net emissions (−73 to 279 ng m^{−2} h^{−1} across 161 individual measurements), and with no strong seasonality, but with time-averaged net emission overall [27 ± 57 (1 SD)] ng m^{−2} h^{−1}. This work demonstrates that scale-up needs to be based on sufficient individual measurements to provide a reasonably constrained estimate of the long-term mean. Mean (± 1 SD) net CH₃Br emissions from deciduous and coniferous leaf litter were 43 (± 33) ng kg^{−1} (dry weight) h^{−1} and 80 (± 37) ng kg^{−1} (dry weight) h^{−1}, respectively, and ~ 1–2 ng kg^{−1} (fresh weight) h^{−1} from rotting woody litter. Despite the intrinsic variability, data obtained here consistently point to the conclusion that the temperate forest soil/litter ecosystem is a net source of CH₃Br to the atmosphere.

Keywords: CH₃Br, emissions, enclosure, flux, litter, ozone layer, Scotland, woodland

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Introduction

Methyl bromide (CH₃Br) is a trace gas emitted to the troposphere from various sources, including fugitive release from pesticide fumigation, biomass burning, the ocean and rice paddies, wetlands and salt marshes. The lifetime of CH₃Br in the atmosphere is sufficiently long [current best estimate 0.7 years (WMO, 2007)] that a significant proportion can reach the stratosphere, where, via the Br radical released by photolysis, it is a major contributor to stratospheric ozone loss processes. Because it is estimated that CH₃Br contributes ~ 37%

of all Br reaching the stratosphere (WMO, 2007), the deliberate use of CH₃Br (principally as a soil fumigant) is being phased out under the Montreal Protocol. Other anthropogenic sources of CH₃Br include biomass burning and fossil fuel combustion but are small compared with estimates of its natural fluxes from terrestrial and marine ecosystems (WMO, 2007). The latter are estimated to contribute at least half of the CH₃Br reaching the stratosphere, but there is considerable uncertainty in quantifying the natural fluxes because of the paucity of data on process mechanisms and extent of variability. In the WMO evaluation, the estimated global total sink flux of CH₃Br (204 Gg yr^{−1}) exceeds the total global source flux (159 Gg yr^{−1}) by approximately one-quarter (WMO, 2003), but with very large uncertainties in each estimate (129–387 and 77–293 Gg yr^{−1}, respectively). The most recent WMO (2007) assessment does not report any resolution of the CH₃Br source/sink

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discrepancy. Modelling studies have suggested the imbalance cannot be explained by the large range of uncertainty (Reeves, 2003) but is due to unidentified natural sources rather than due to sink terms that have been overestimated (Saltzman *et al.*, 2004; Warwick *et al.*, 2006). Natural terrestrial sources of CH₃Br are particularly poorly identified and quantified.

The lack of CH₃Br budget closure is important: first, global atmospheric chemistry models require quantitative data on all CH₃Br sources/sinks for accurate prediction of the trajectory of stratospheric ozone levels; second, many natural CH₃Br sources/sinks are directly and indirectly influenced by human activity, most notably via changes in land cover and use, including potentially as a consequence of future climate change. In addition, as anthropogenic phase-out of CH₃Br continues, the magnitudes of natural fluxes of CH₃Br may become relatively more important. Among these natural sources, forest and woodlands have been identified as potentially important sources, but also sinks of CH₃Br (Shorter *et al.*, 1995; Serça *et al.*, 1998; Lee-Taylor & Holland, 2000; Dimmer *et al.*, 2001; Rhew *et al.*, 2003; Varner *et al.*, 2003). The information on temperate woodlands is limited, but because their global area is very large, CH₃Br fluxes from this ecosystem have the potential to contribute significantly to the global CH₃Br budget. In this research, long-term measurements of CH₃Br net flux from four field enclosure chambers in a temperate woodland in Scotland were made from March 2005 to August 2006, providing a dataset of 161 individual measurements, substantially larger than previous studies. Relationships between net fluxes and environmental variables such as air and soil temperature and methane net flux were examined to explore the processes influencing CH₃Br emissions. Rotting wood, deciduous leaf and coniferous needle litter were also investigated to determine potential net fluxes of CH₃Br from these substrates.

Materials and methods

Field measurements

Four collars (internal diameter 24 cm) for enclosure chambers made of opaque hard plastic (PVC) and with a headspace volume of 0.0058 m³ were set up permanently in the Hermitage of Braid woodland (55°55'N, 3°12'W), a local nature reserve of 53 ha in southern Edinburgh, Scotland. The seminatural woodland dates to the early 19th century and is dominated by beech (*Fagus sylvatica*), ash (*Fraxinus excelsior*) and sycamore (*Acer pseudoplatanus*). The collars were arranged as replicate pairs about 3 m apart within two contrasting areas of vegetation in the woodland. Collars I1 and I2

were placed in ivy (*Hedera helix*) covered ground beneath trees at the top of a slope, and collars B3 and B4 were placed in a beech dominated area underlain by a sparse coverage of leaf litter. Occasionally, small plants such as willowherb (*Epilobium spec.*) or bramble (*Rubus fruticosus*) grew inside the collars for a few weeks. There were no distinctive differences in soil properties between the two areas. The soil was a sandy loam with a mean pH of 5.5 ($n = 4$) and a mean organic matter content in the top 10 cm, derived by loss after ignition at 500 °C, of 10% (w/w) oven-dry soil ($n = 4$). Water-extractable soil Br⁻ content was below the detection limit of 1.4 µg Br⁻ g⁻¹ dry weight soil.

For gas sampling, the collars were enclosed with gas-tight aluminium lids for only short periods (10 min) so as not to influence vegetation and soil within the collars. At the end of the enclosure, a 400 mL air sample from the headspace was extracted into a 1000 mL gas-tight syringe via a tap in the centre of the lid and transferred to a pre-evacuated 1 L Tedlar bag. Sample bags were stored in the dark at room temperature until analysis on the same day or within 24 h. Experiments showed no loss of CH₃Br under these storage conditions. On each sampling occasion, measurements were also made of the air temperature and the soil temperature at 10 cm depth immediately adjacent to the chambers. Samples were taken every 1–2 weeks between March 2005 and August 2006.

Samples of deciduous leaf litter, primarily of *A. pseudoplatanus* (sycamore), were collected from the woodland floor near the enclosure collars on five occasions between November and December 2005, and on four occasions between November 2006 and January 2007. A substantial proportion of leaf litter was noted to be infected with the *Rhizyctis* fungus. As soon as possible after collection, between two and eight subsamples of each bulk sample were enclosed separately in an opaque plastic container of 10 L volume and headspace air was withdrawn after a fixed time interval through a three-way tap in the lid. Enclosures of the empty container only showed no measurable CH₃Br flux. Net fluxes were also measured in the same manner from samples of needle litter of *Picea sitchensis* (Sitka spruce) and *Pinus sylvestris* (Scots pine) collected at intervals during 2006 from nearby conifer forests, and from three samples of rotting beech wood collected from the deciduous woodland floor.

Gas analysis

The CH₃Br was quantified using an HP 5890 gas chromatograph equipped with an electron capture detector and a DB624 capillary column (J&W Scientific, Folsom, CA, USA; 30 m long, 0.32 mm i.d., 1.8 µm film

thickness). The temperature programme was 40 °C for 5 min, ramping at 40 °C min⁻¹ to 240 °C and hold for 5 min. Ten percent methane in argon was used for both the carrier gas (flow rate 1.3 mL min⁻¹) and the make-up gas for the electron capture detector (flow rate 25 mL min⁻¹). A two-trap preconcentration unit was used before GC separation in order to quantify CH₃Br mixing ratios to lower than 10 pptv (Drewer *et al.*, 2006). The first trap was a 1/4 inch stainless steel tube filled with 0.59 g of Tenax (Sigma Aldrich, UK), which was Peltier-cooled to -4 °C during sample loading to enhance the efficiency of adsorption. The sample was then transferred by heating to the second trap, which consisted of 20 cm of 1/8 inch stainless steel tubing filled with fine glass beads and cooled to -79 °C using dry ice. Calibration standards covering a concentration span within the range 10–1000 pptv appropriate to the samples being analysed were prepared volumetrically in air using a certified 500 ppbv CH₃Br standard in nitrogen (Air Products Inc., Allentown, PA, USA). The average analytical relative error in CH₃Br quantification for sample concentrations analysed was evaluated to be ±15% (with higher uncertainty for the lowest concentrations quantified). The detection limit for quantification of net flux was 12 ng m⁻² h⁻¹, derived from the minimum detectable change in CH₃Br concentration of 4 pptv from that in ambient air. Limits of detection for net fluxes from the deciduous and coniferous litter enclosures were determined to be 24 and 10 ng kg⁻¹ (dry weight) h⁻¹, respectively.

Some enclosure headspace samples were also analysed for methane (CH₄) using a separate HP 5890 gas chromatograph equipped with a flame ionisation detector (GC-FID). Separation was on a 1/8 inch packed column (Porapak QS 80–100 mesh, Sigma Aldrich, UK) at 50 °C with injector and detector temperatures of 70 and 250 °C, respectively. Gas flow rates were 21 mL min⁻¹ for the nitrogen carrier, and 25 and 63 mL min⁻¹, respectively, for the hydrogen and air for the FID. The Tedlar bags containing the gas samples were connected via luer fittings to an automated injection system fitted to the GC.

Results

Time series of woodland soil net flux

The net CH₃Br flux from the woodland chambers fluctuated between positive (emission) and negative (uptake) (Fig. 1a). A summary of fluxes from each chamber separately and combined over the whole measurement period is shown in Table 1. The mean measured net flux from the chambers varied between 17 and 33 ng m⁻² h⁻¹, with an overall mean of all mea-

sured fluxes of 27 ± 57 (1 SD) ng m⁻² h⁻¹ (*n* = 161). The median measured net flux from the chambers varied between 5 and 18 ng m⁻² h⁻¹, with an overall median of all measured fluxes of 8 ng m⁻² h⁻¹. There was no significant statistical difference (MANOVA) in flux with time between the two types of woodland location (chambers I and chambers B). In general, the net fluxes from the four chambers exhibited the same variation between one measurement occasion and another, but superimposed on this were clear instances of considerably higher emissions from individual chambers at particular times. There was no discernible pattern to these excursions, or relationship to other measured or observable features at the monitoring locations, except that the prolonged period of net emissions from chamber B3 between July and September 2005, when all the other chambers exhibited zero or small uptake flux, coincided with the growth of an *Epilobium* spec. (willowherb) within the collar.

Even though fluxes fluctuated between net uptake and net emission, the mean/median net flux over the whole measurement period was emission. Recalculating mean fluxes using zero for all fluxes smaller than the net flux detection limit of 12 ng m⁻² h⁻¹ did not change the mean net emission values shown in Table 1 by more than ± 2 ng m⁻² h⁻¹.

There was no apparent seasonal pattern in fluxes from these chambers (although, see later for discussion of fluxes in relation to temperature). Overall mean fluxes were similar in winter [25 ± 75 (1 SD) ng m⁻² h⁻¹, October to February] and summer (28 ± 50 ng m⁻² h⁻¹, March to September). Overall median flux in winter (0 ng m⁻² h⁻¹) was lower than the median flux of 18 ng m⁻² h⁻¹ for the two summer periods, but the means were similar because of the predominance of the short-term excursions of higher emissions in winter.

From May 2005 to June 2006, air samples from the woodland chamber enclosures were also analysed for CH₄ in order to investigate whether there was any relationship between CH₄ and CH₃Br net fluxes (Fig. 1b). Net CH₄ fluxes were three orders of magnitude greater than net CH₃Br fluxes and were mainly negative, with uptake generally a few tens of μg m⁻² h⁻¹, but increasing to about 150 μg m⁻² h⁻¹ in autumn. The time series of net CH₄ fluxes were generally similar for all four chambers. On the few occasions on which net emissions of CH₄ were measured, soil conditions were very wet and thus presumed anaerobic. Mean (1SD) measured net CH₄ fluxes for individual chambers ranged between -30 (35) and -40 (39) μg m⁻² h⁻¹, with an overall mean net flux of -34 (46) μg m⁻² h⁻¹. Median measured net CH₄ fluxes for individual chambers ranged between -17 and -28 μg m⁻² h⁻¹, with an overall median net flux of -21 μg m⁻² h⁻¹. Thus, overall, there

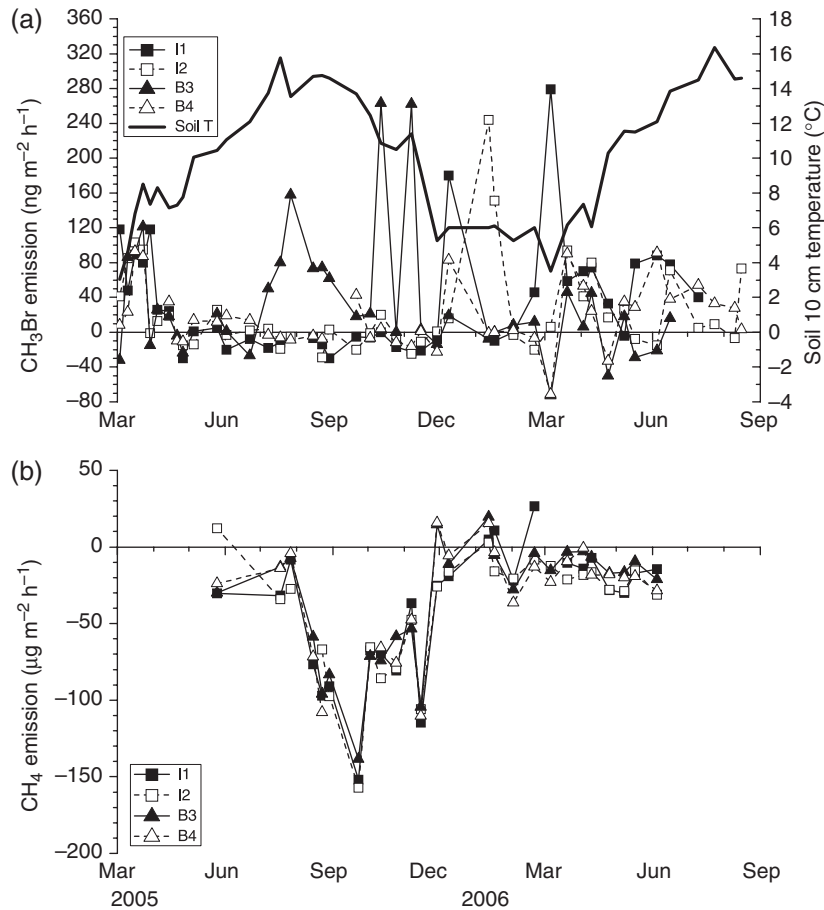


Fig. 1 Net fluxes of CH₃Br (a) and CH₄ (b) at four locations in deciduous woodland measured between March 2005 and August 2006. Data for B3 cease in mid-June 2006 when the chamber disappeared, presumed stolen. The limit of detection of net CH₃Br flux was calculated to be $\pm 12 \text{ ng m}^{-2} \text{ h}^{-1}$. The solid line in part (a) shows the 10 cm depth soil temperature.

Table 1 Summary of CH₃Br net fluxes measured from four woodland enclosures between March 2005 and August 2006

Chamber	Net flux of CH ₃ Br/ng m ⁻² h ⁻¹				
	I1	I2	B3	B4	All
<i>n</i>	39	42	39	41	161
Mean	33	25	33	17	27
Median	1	5	18	8	8
SD	64	54	71	36	57
Range	-30 to 279	-29 to 244	-73 to 263	-71 to 93	-73 to 279

was net uptake of CH₄ for the year of measurements. Methane fluxes measured at this woodland site were within the range for seven UK woodland sites of -135 to $+45 \mu\text{g m}^{-2} \text{ h}^{-1}$ reported by Smith *et al.* (2000). A pairwise scatter plot (not shown) of the data in Figs 1a and b showed there was no quantitative relationship between measured CH₃Br and CH₄ fluxes. This suggests that different processes are involved in CH₄ and CH₃Br

production and uptake, as noted previously in other terrestrial systems (White *et al.*, 2005; Rhew *et al.*, 2007).

There were no strong relationships between CH₃Br fluxes from the individual chambers and soil temperature (which differed very little from air temperature because of the canopy shading). There was a slight trend for greater net CH₃Br emissions from chambers I1 and I2 at cooler temperatures and for higher emissions from chamber B3 to be associated with warmer temperatures (Fig. 2). The reasons for the difference are unknown.

Diurnal measurements of CH₃Br fluxes were made at each enclosure on one day in summer and one day in winter, as shown in Fig. 3. The associated soil and air temperatures varied only slightly during the days on which flux measurements were carried out, remaining in the ranges of 14–15 and 14–18 °C, respectively, for the summer measurements and the ranges of 5–6 and 4–7 °C, respectively, for the winter measurements.

Net CH₃Br flux from enclosure B3 in the summer diurnal measurement series showed the same high emissions that were observed in the series of regular

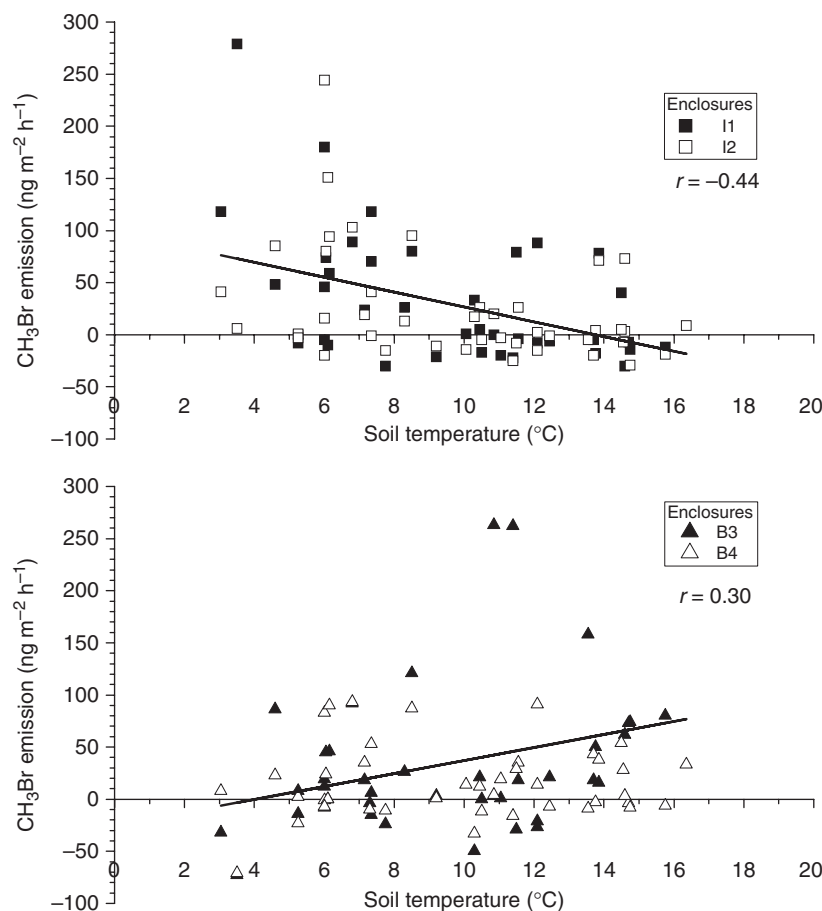


Fig. 2 Net CH_3Br flux as a function of 10 cm depth soil temperature at time of sampling for the four woodland chambers throughout the measurement period, March 2005 to August 2006.

weekly or two-weekly measurements being made around this time (Fig. 1a) and may have been associated with the growth of a willowherb plant within the enclosure. The net emission from this enclosure peaked around midday, and was therefore consistent with an association with the diurnal cycle as reported for CH_3Br emissions from a nearby vegetated salt marsh (Drewer *et al.*, 2006). The diurnal fluxes from the other three enclosures were close to, or below, the limit of detection, also consistent with the regular time series measurements from these chambers around this time, as were the fluxes during the winter diurnal measurements.

Fluxes from woody and nonwoody litter

Mean net CH_3Br fluxes from the subsamples of deciduous and coniferous litter collected on each sampling occasion are shown in Figs 4 and 5, respectively. The mean (1 SD) net flux from the coniferous needle litter of 80 (37) ng kg^{-1} (dry weight) h^{-1} ($n = 7$ sampling occasions) was approximately double the mean net flux

from the deciduous leaf litter of 43 (33) ng kg^{-1} (dry weight) h^{-1} ($n = 9$ sampling occasions). The magnitudes of the standard deviations plotted in Figs 4 and 5 show there was frequently a wide variation in the measured fluxes between the subsamples of a single bulk sample. Despite this heterogeneity, net CH_3Br fluxes from litter were persistently positive (emission) overall, with fluxes from the deciduous leaf litter showing a persistent decline throughout the late autumn and winter in both years of sampling, presumably related to changing rates of litter decay. Fluxes from the coniferous needle litter did not show seasonal variation exceeding the within-sample variation of subsample replicates. Overall, these data show that decaying temperate deciduous and coniferous litter are both net sources of CH_3Br that need to be considered in a global budget.

Net CH_3Br fluxes from subsamples of the three samples of rotting beech wood were low. Apart from an emission of 16 ng kg^{-1} (fresh weight) h^{-1} measured on one occasion, other measured net fluxes were close to or below the limit of detection, calculated to be

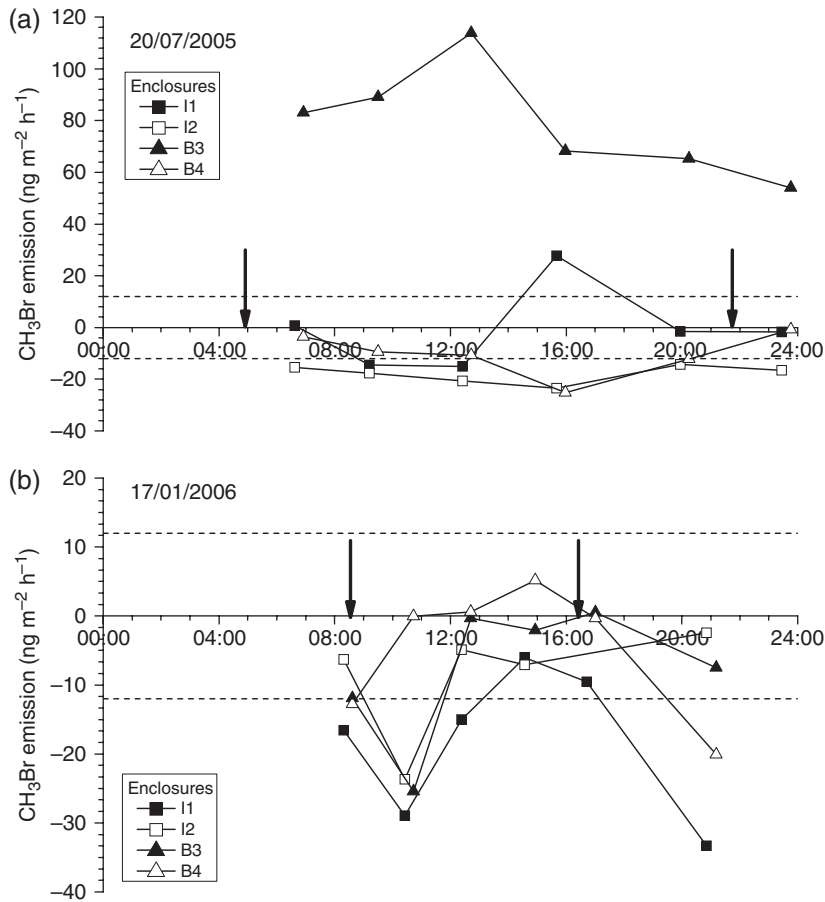


Fig. 3 Diurnal fluxes of CH₃Br measured at the four deciduous woodland enclosures on a day in summer (a) and winter (b). The pair of arrows on each figure mark the times of local sunrise and sunset. The dashed lines indicate the limit of detection of a net CH₃Br flux.

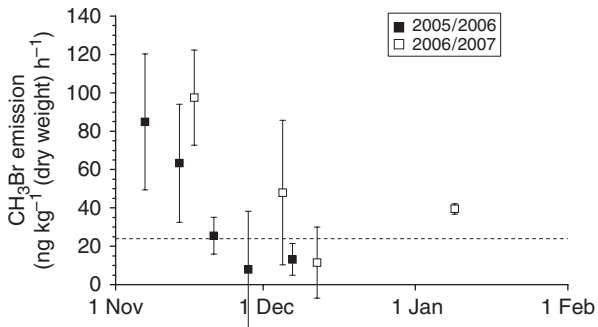


Fig. 4 Net CH₃Br flux measured from two to eight subsamples of deciduous leaf litter from the Hermitage woodland in Edinburgh during two autumn/winter periods. Data values are mean ± 1 SD of the subsamples. The dashed line marks the detection limit for quantifying a net flux in these measurements.

1.6 ng kg⁻¹ (fresh weight) h⁻¹ net flux for these measurements. In a further experiment, two subsamples with visible fungi from the same rotting log were enclosed on four occasions over 3 days at laboratory temperature and the visible fungi material were then

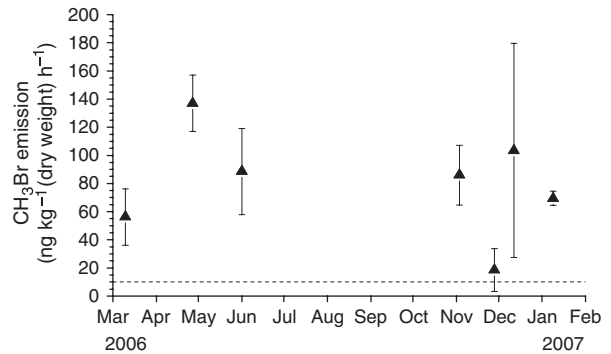


Fig. 5 Net CH₃Br flux measured from two to four subsamples of coniferous needle litter from two forests (March–June 2006, Griffin Forest, Perthshire; November 2006–January 2007, Hermitage, Edinburgh). Data values are mean ± 1 SD of the subsamples. The dashed line marks the detection limit for quantifying a net flux in these measurements.

removed and the fluxes remeasured for a further 2 days. Flux from one sample was lower after fungi removal, but measured fluxes from the other sample were generally below the calculated detection limit.

Table 2 Summary of data from this work and reported in the literature of net fluxes of CH₃Br from woodland ecosystems

Reference	Location	Type of study	CH ₃ Br flux determination	No. of measurements
Shorter <i>et al.</i> (1995)	Durham, NH, USA (43°08'N, 71°57'W)	CH ₃ Br-dosed field enclosures at a mixed deciduous and conifer forest	-22 Gg yr ⁻¹ global temperate woodland	Not given
Serça <i>et al.</i> (1998)	Denver, CO, USA	CH ₃ Br-dosed field enclosures at a cottonwood and deciduous shrub site	-38 ± 30 Gg yr ⁻¹ global temperate woodland	Not given
Lee-Taylor & Holland (2000)	-	Modelling study using estimates for litter decay, bromide content and fungal CH ₃ Br production	+1.7 (0.5–5.2) Gg yr ⁻¹ global aboveground woody litter ~ +4 Gg yr ⁻¹ global aboveground fine litter	-
Rhew <i>et al.</i> (2003)	Soils from three sites in AK, USA	Laboratory incubations with isotopically labelled CH ₃ Br	-39 (± 11) ng m ⁻² h ⁻¹ * uptake +9.9 (± 5.5) ng m ⁻² h ⁻¹ * emission	9 9
Dimmer <i>et al.</i> (2001)	Galway, Ireland (53°19'N, 9°54'W)	Ambient field enclosures at two conifer plantations on peat	+190 (+30 to +740) ng m ⁻² h ⁻¹ † (no global estimate provided)	14
Varner <i>et al.</i> (2003)	Durham, NH, USA (43°08'N, 71°57'W)	Ambient field enclosures at a mixed deciduous and conifer forest	-30 (-170 to +140) ng m ⁻² h ⁻¹ ‡ -2.2 ± 0.9 Gg yr ⁻¹ global temperate woodland	28
This work	Edinburgh, Scotland, UK 55°55'N, 3°12'W	Ambient field enclosures at a deciduous wood on sandy loam deciduous leaf litter coniferous needle litter rotting wood	+27 (+17 to +33) ng m ⁻² h ⁻¹ § +43 (+8 to +98) ng kg ⁻¹ dry weight h ⁻¹ ¶ +80 (+19 to +137) ng kg ⁻¹ dry weight h ⁻¹ ¶ +1.6 ng kg ⁻¹ fresh weight h ⁻¹	161 35 19 10

*Converted from authors' reported units of nmol m⁻² day⁻¹.

†Converted from authors' reported units of g m⁻² yr⁻¹.

‡Converted from authors' reported units of µg m⁻² day⁻¹.

§Quoted range is minimum and maximum of the mean flux from four enclosures, March 2005 to August 2006.

¶Quoted range is minimum and maximum of the mean flux of subsample replicates.

Discussion

Table 2 compares the data for CH₃Br fluxes obtained from the woodland matrices studied here with the few data reported in the literature for this ecosystem. The current study comprises a considerably higher number of individual measurements, made over a much longer time period, than previous studies. Shorter *et al.* (1995) and Serça *et al.* (1998) reported results from *in situ* CH₃Br uptake experiments over forest soils using enclosures into which CH₃Br was injected. Both studies found rapid CH₃Br uptake, from which were estimated global sink fluxes for CH₃Br in temperate forest soils of 22 and 38 ± 30 Gg yr⁻¹, respectively. Rhew *et al.* (2003)

incubated samples of boreal forest soil in the lab with isotopically labelled CH₃Br and determined that CH₃Br uptake flux exceeded production flux, with a net uptake on average of 0.71 µg m⁻² day⁻¹ (30 ng m⁻² h⁻¹). These enclosure studies used initial CH₃Br mixing ratios up to three orders of magnitude greater than ambient (in the range a few 100 pptv to 5 ppbv) and do not address the issue of net flux from forest soil under unperturbed, ambient conditions. To our knowledge, only two published studies do. Dimmer *et al.* (2001) reported median net CH₃Br emission equivalent to 190 ng m⁻² h⁻¹ (range in individual measurements 30–740 ng m⁻² h⁻¹) from two enclosures on peaty soils under conifer plantation in Galway, Ireland, for *n* = 14 measurements in

September; Varner *et al.* (2003) reported mean net CH₃Br uptake equivalent to 30 ng m⁻² h⁻¹ (range in individual measurements from 170 ng m⁻² h⁻¹ net uptake to 140 ng m⁻² h⁻¹ net emission) from two enclosures in mixed woodland in New Hampshire, USA, for *n* = 28 measurements between May and September. Thus, as with the current study, both these earlier studies reported a wide range in fluxes (both uptake and emission) from individual measurements. The spatial and temporal variabilities of measured woodland CH₃Br fluxes may reflect sensitivity of net flux to variation in larger consumption and production processes occurring at the same time. On average, however, Varner *et al.* (2003) report a net uptake flux while Dimmer *et al.* (2001) report a net emission flux. Our measurements also indicate a net emission flux, on average, from temperate woodland soil and litter, although of a smaller magnitude than that of Dimmer *et al.* (2001). The mean (1 SD) flux during the 18 months of regular measurement at the four below-canopy sites in this work was 27 (57) ng m⁻² h⁻¹. In the absence of any clearly discernible seasonal or diurnal trend in the measurements, it is reasonable to take the overall mean as the best estimate for annual average net soil flux at this woodland. This yields an annual CH₃Br net emission of 240 (500) µg m⁻². The lower values here than those of Dimmer *et al.* (2001) may be because our measurements are averaged over an entire year whereas those of Dimmer *et al.* (2001) were from late summer only.

One specific likely source of CH₃Br in woodland ecosystems is fungal activity, in particular the *Hymenochaetaceous* genera ('white rot' fungi), acting on woody and nonwoody litter on the forest floor. Laboratory studies on these fungi have mainly focused on CH₃Cl production (Harper & Hamilton, 1988; Harper *et al.*, 1988; Harper, 1998), but it has also been shown that Br is preferentially methylated over Cl (Harper, 1985; Harper & Kennedy, 1986). One field study has reported CH₃Cl emissions from enclosures of rotting wood in a tropical forest (Moore *et al.*, 2005), but these workers did not investigate CH₃Br fluxes. Our experiment with fungus on rotting wood is consistent with this as a source. There is also literature evidence that the ectomycorrhizal fungi associated with tree roots may be an important source of methyl halides to the atmosphere (Redeker *et al.*, 2004). This is again consistent with the small net flux, on average, from our chambers over woodland soil. The data we present here for *in situ* emissions of CH₃Br from leaf litter (which may likewise be associated with fungal activity) are, to the best of our knowledge, the only such data currently available.

A global emission flux for temperate woodland has previously not been included in global budgets of

CH₃Br. Although the literature contains examples of global upscaling of single-location measurements of CH₃Br fluxes from various terrestrial systems (for example, Varner *et al.*, 1999; Rhew *et al.*, 2000, 2007; Dimmer *et al.*, 2001; Varner *et al.*, 2003; Drewer *et al.*, 2006; Mead *et al.*, 2008), it would be speculative to extrapolate our measurement of average net CH₃Br flux to the area of all temperate woodland globally. Instead, we note here the global scale of this biome. Summing the land cover estimates for ecosystem classification types 4, 5, 8 and E defined by Matthews (1983) yields an area for temperate woodlands worldwide of 13 × 10¹² m². Estimates for aboveground litter pools in temperate woodland vary widely but are in the range of 2–4 kg (dry weight) litter m⁻², being toward the higher end of this range for temperate latitude continental interiors and towards the lower end for higher latitudes (Matthews, 1997). Approximately 30% of the litter pool is assigned to herbaceous (nonwoody) litter, and 70% to woody detritus. This yields estimates of 8–16 and 18–36 Pg, respectively, for the masses of nonwoody and woody litter pools in temperate forests globally. Thus, although the average net fluxes from the woodland and associated litter were much lower than those from a nearby salt marsh (Drewer *et al.*, 2006), they have the potential to be important globally because of the considerably greater area of temperate woodlands worldwide compared with salt marsh [0.38 × 10¹² m² (Woodwell *et al.*, 1973)].

Conclusions

The CH₃Br fluxes from deciduous woodland soil, rotting wood and deciduous and coniferous litter reported here from an 18 month measurement campaign constitute the most detailed dataset available for temperate woodland. Although point measurements of net flux are inevitably subject to considerable spatial and temporal variability, a consistent net positive flux (i.e. emission) of CH₃Br from temperate deciduous forest floor (and deciduous and coniferous aboveground litter) has been demonstrated in this work. This is in contrast to some previous literature reports of net uptake of CH₃Br by temperate forest soil, and implies that temperate woodland may currently be overlooked as a source of CH₃Br. Qualitatively, even quite small net emission fluxes of CH₃Br from temperate woodland ecosystems may be important globally because of their large area worldwide. However, a quantitative assessment of global CH₃Br flux will require accumulation, and appropriate combination, of data from a range of temperate woodland environments worldwide.

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References

- Dimmer CH, Simmonds PG, Nickless G, Bassford MR (2001) Biogenic fluxes of halomethanes from Irish peatland ecosystems. *Atmospheric Environment*, **35**, 321–330.
- Drewer J, Heal MR, Heal KV, Smith KA (2006) Temporal and spatial variation in methyl bromide emissions from a salt marsh. *Geophysical Research Letters*, **33**, L16808, doi: 10.1029/2006GL026814.
- Harper DB (1985) Halomethane from halide ion – a highly efficient fungal conversion of environmental significance. *Nature*, **315**, 55–57.
- Harper DB (1998) Biosynthesis and utilization of chloromethane by fungi. *Journal of Chemical Technology and Biotechnology*, **71**, 366–367.
- Harper DB, Hamilton JTG (1988) Biosynthesis of chloromethane in *Phellinus-Pomaceus*. *Journal of General Microbiology*, **134**, 2831–2839.
- Harper DB, Kennedy JT (1986) Effect of growth conditions on halomethane production by *Phellinus* species – biological and environmental implications. *Journal of General Microbiology*, **132**, 1231–1246.
- Harper DB, Kennedy JT, Hamilton JTG (1988) Chloromethane biosynthesis in Poroid fungi. *Phytochemistry*, **27**, 3147–3153.
- Lee-Taylor JM, Holland EA (2000) Litter decomposition as a potential natural source of methyl bromide. *Journal of Geophysical Research – Atmospheres*, **105**, 8857–8864.
- Matthews E (1983) Global vegetation and land-use – new high-resolution data-bases for climate studies. *Journal of Climate and Applied Meteorology*, **22**, 474–487.
- Matthews E (1997) Global litter production, pools, and turnover times: estimates from measurement data and regression models. *Journal of Geophysical Research – Atmospheres*, **102**, 18771–18800.
- Mead MI, Khan MAH, Nickless G, Grealley BR, Tainton D, Pitman T, Shallcross DE (2008) Leaf cutter ants: a possible missing source of biogenic halocarbons. *Environmental Chemistry*, **5**, 5–10.
- Moore RM, Gut A, Andreae MO (2005) A pilot study of methyl chloride emissions from tropical woodrot fungi. *Chemosphere*, **58**, 221–225.
- Redeker KR, Treseder KK, Allen MF (2004) Ectomycorrhizal fungi: a new source of atmospheric methyl halides. *Global Change Biology*, **10**, 1009–1016.
- Reeves CE (2003) Atmospheric budget implications of the temporal and spatial trends in methyl bromide concentration. *Journal of Geophysical Research – Atmospheres*, **108**, 4343, doi: 10.1029/2002JD002943.
- Rhew RC, Aydin M, Saltzman ES (2003) Measuring terrestrial fluxes of methyl chloride and methyl bromide using a stable isotope tracer technique. *Geophysical Research Letters*, **30**, 2103, doi: 10.1029/2003GL018160.
- Rhew RC, Miller BR, Weiss RF (2000) Natural methyl bromide and methyl chloride emissions from coastal salt marshes. *Nature*, **403**, 292–295.
- Rhew RC, Teh YA, Abel T (2007) Methyl halide and methane fluxes in the northern Alaskan coastal tundra. *Journal of Geophysical Research – Biogeosciences*, **112**, G02009, doi: 10.1029/2006JG000314.
- Saltzman ES, Aydin M, De Bruyn WJ, King DB, Yvon-Lewis SA (2004) Methyl bromide in preindustrial air: measurements from an Antarctic ice core. *Journal of Geophysical Research – Atmospheres*, **109**, D05301, doi: 10.1029/2003JD004157.
- Serça D, Guenther A, Klingner L, Helmig D, Hereid D, Zimmerman P (1998) Methyl bromide deposition to soils. *Atmospheric Environment*, **32**, 1581–1586.
- Shorter JH, Kolb CE, Crill PM, Kerwin RA, Talbot RW, Hines ME, Harriss RC (1995) Rapid degradation of atmospheric methyl-bromide in soils. *Nature*, **377**, 717–719.
- Smith KA, Dobbie KE, Ball BC *et al.* (2000) Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystems, and uncertainties in the global terrestrial sink. *Global Change Biology*, **6**, 791–803.
- Varner RK, Crill PM, Talbot RW (1999) Wetlands: a potentially significant source of atmospheric methyl bromide and methyl chloride. *Geophysical Research Letters*, **26**, 2433–2435.
- Varner RK, White ML, Mosedale CH, Crill PM (2003) Production of methyl bromide in a temperate forest soil. *Geophysical Research Letters*, **30**, 1521, doi: 10.1029/2002GL016592.
- Warwick NJ, Pyle JA, Shallcross DE (2006) Global modelling of the atmospheric methyl bromide budget. *Journal of Atmospheric Chemistry*, **54**, 133–159.
- White ML, Varner RK, Crill PM, Mosedale CH (2005) Controls on the seasonal exchange of CH₃Br in temperate peatlands. *Global Biogeochemical Cycles*, **19**, GB4009, doi: 10.1029/2004GB002343.
- WMO (2003) *Scientific Assessment of Ozone Depletion: 2002 Global Ozone Research and Monitoring Project Report No. 47*. World Meteorological Organization, Geneva.
- WMO (2007) *Scientific Assessment of Ozone Depletion: 2006 Global Ozone Research and Monitoring Project Report No. 50*. World Meteorological Organization, Geneva.
- Woodwell GM, Rich PH, Hall CAS (1973) In: *Carbon and the Biosphere* (eds Woodwell GM, Pecan EV), pp. 221–240. Brookhaven Symposia in Biology 24, US Atomic Energy Commission, Washington, DC.