

# Methyl bromide and methyl chloride fluxes from temperate forest litter

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## Abstract

Methyl halide fluxes were measured from fine (nonwoody) litter samples in a temperate deciduous forest site in Scotland on 16 occasions over more than a year and from a coniferous forest site. The resulting mean ( $\pm 1$  sd)  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  fluxes were  $4.1 \pm 3.7 \text{ ng kg}^{-1} \text{ h}^{-1}$  and  $0.98 \pm 0.62 \text{ } \mu\text{g kg}^{-1} \text{ h}^{-1}$ , respectively, for dry mass leaf litter and  $5.7 \pm 6.3 \text{ ng kg}^{-1} \text{ h}^{-1}$  and  $0.47 \pm 0.14 \text{ } \mu\text{g kg}^{-1} \text{ h}^{-1}$  for dry mass needle litter. Temporal variations of net fluxes from leaf litter were significantly greater than spatial variations suggesting seasonality in the fluxes. The mean  $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$  mass ratio of fluxes was  $\sim 200$ , an order of magnitude larger than the ratio of their estimated global turnovers. Temperate forest litter may be a moderate net source of  $\text{CH}_3\text{Cl}$  globally but a negligible source of  $\text{CH}_3\text{Br}$ . These statements refer to the nonwoody litter component only.

*Keywords:* methyl halides, leaf litter, temperate, forest

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## 1. Introduction

During the last few years a persistent shortfall in estimates of known sources against known sinks of global  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  budgets has been noted, with up to a quarter of the emissions of these two gases needed to balance the global budgets not accounted for with currently available data (Montzka et al., 2002; Clerbaux et al., 2007; Yvon-Lewis et al., 2009). These

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7 two methyl halide gases are the main natural vectors of bromine and chlorine  
8 into the stratosphere, where they account for 37 % and 16 % of bromine and  
9 chlorine related ozone loss, respectively (Fahey, 2007).

10 Amongst many others, leaf litter has been proposed as a potential glo-  
11 bally important source of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  (Watling and Harper, 1998;  
12 Lee-Taylor and Holland, 2000; Hamilton et al., 2003; Drewer et al., 2008;  
13 Wishkerman et al., 2008) but has not been widely studied. This study was  
14 therefore established to examine the potential impact of leaf litter from tem-  
15 perate forests on global methyl halide budgets.

16 Temperate forests are estimated to account for a global land area of  
17  $27.9 \times 10^{12} \text{ m}^2$  (UNESCO, 1973; Matthews, 1997) and have the potential to  
18 produce or to remove large amounts of methyl halides through a number  
19 of sources and sinks. Potential sources include higher plants (Drewer et al.,  
20 2008), forest soils (Dimmer et al., 2001; Drewer et al., 2008), litter (Hamilton  
21 et al., 2003; Drewer et al., 2008; Wishkerman et al., 2008), and the fungi often  
22 associated with litter (Watling and Harper, 1998; Lee-Taylor and Holland,  
23 2000) whilst reported sinks comprise forest soils (Serca et al., 1998; Rhew  
24 et al., 2003) and higher plants (Jeffers et al., 1998).

25 Of these four forest components (plants, soils, litter and fungi) this study  
26 concentrates on small nonwoody detritus (leaves and needles). The reason  
27 for this interest is that even small fluxes per unit mass could result in si-  
28 zeable global fluxes when considering the large extent of temperate forest  
29 cover. Moreover, there are to date no field data on  $\text{CH}_3\text{Cl}$  fluxes from tem-  
30 perate forest litter although it has been shown to be a potentially important  
31 source of  $\text{CH}_3\text{Br}$  by our group (Drewer et al., 2008), from measurements  
32 made during autumn and winter. Another study by our group in Borneo,  
33 SE Asia, estimated that  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  net flux from tropical forest leaf  
34 litter could account for  $\sim 0.1$  % and  $\sim 7$  % of the respective global budgets  
35 (Blei et al., 2010a). It is also of interest to examine if any potential source  
36 is seasonal to improve information for extrapolation to global budgets.

37 Two laboratory studies examining the possibility of abiotic production  
38 of methyl halides by Hamilton et al. (2003) and Wishkerman et al. (2008)  
39 reported that  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  fluxes negatively correlate with leaf litter  
40 water content and this was also investigated in this work.

## 41 2. Field locations

42 The main field location was Fir Links forest, a 2.05 ha mixed beech (*Fagus*  
43 *sylvatica*) and sycamore (*Acer pseudoplatanus*) woodland planted in 1954,  
44 situated adjacent to the North Sea coastline within the John Muir Country  
45 Park, East Lothian, Scotland (56°0.1'N 002°35.7'W). The site is not cleared  
46 of smaller debris and has a perennial layer of leaf litter. During the study,  
47 ground vegetation was either sparse or absent and consisted of ferns of varying  
48 density. Topographically the site had very few features, being situated on  
49 a plateau a few metres above sea level. 124 enclosures on 76 samples were  
50 taken on 16 occasions starting on the 30<sup>th</sup> April 2008 until the 28<sup>th</sup> July 2009.

51 The second site was Griffin Forest (56°37'N 003°38'W), a Sitka spruce (*Pi-*  
52 *cea sitchensis*) plantation of 3862 ha planted in 1981, situated 350 m above  
53 sea level near the town of Aberfeldy in Perthshire, Scotland (Ibrom et al.,  
54 2006). Ten samples were taken on the 24<sup>th</sup> June 2009, 5 samples each from  
55 a thinned and an un-thinned section of the forest. An earlier attempt to  
56 quantify litter methyl halide fluxes at this site failed due to unexpectedly  
57 high emissions so only data from the one sampling occasion are available.

## 58 3. Methodology

59 Methyl halide fluxes were measured using static enclosures in situ over  
60 durations of 10 min, 1 h, 6 h or 24 h. The different enclosure durations were  
61 used to accommodate different flux strengths and to overcome the dual pro-  
62 blems of non-linear fluxes during long enclosure times and low precisions at  
63 short enclosure times (see later).

### 64 3.1. Enclosures

65 Enclosures were opaque 12 L polypropylene buckets with air-tight lids  
66 and a sampling port made of a 1 mL syringe fitted with an approximately  
67 7 cm long rubber tube that was connected to a three-way valve. Typically  
68 250 to 400 g of fresh leaf/needle litter was placed into each bucket and then  
69 enclosed for either 10 min, 1 h, 6 h or 24 h, after which ~550 mL of headspace  
70 sample was transferred to an empty Tedlar bag which was analysed within a  
71 day or two of collection.

72 Depending on the density of the litter layer on the ground, each sample  
73 represented a few square metres of forest floor litter. The number of buckets  
74 employed for a measurement ranged from 2 to 18 at any time. Except for

75 measurements at Fir Links on the 30<sup>th</sup> April 2008, fluxes were measured  
76 against a blank enclosure. A small temperature data logger monitored the  
77 temperature inside a blank bucket during enclosures.

### 78 *3.2. Determination of fresh mass, dry mass and water content*

79 Sampled leaf/needle litter materials were brought to the laboratory and  
80 the fresh mass recorded. The litter was then placed into paper bags and  
81 dried in an oven at 70 °C to derive dry mass. All water content values are  
82 expressed gravimetrically as % w/w fresh mass.

### 83 *3.3. Correction for litter volumes in enclosures*

84 To acquire an accurate estimate of an enclosed headspace volume the  
85 volume of fresh leaf or needle litter in each was subtracted. Dry litter volumes  
86 were derived by measuring the mean specific volume of oven dried (70 °C)  
87 leaf/needle litter via water displacement on six 50 g replicate samples and  
88 multiplication with the dry masses of the individual litter samples. The dry  
89 litter volume as well as the volume of the water originally contained in the  
90 fresh, wet litter sample was subtracted from the enclosure volume.

### 91 *3.4. Bromine and chlorine content of plant material*

92 Bulk samples of litter material collected from both sites in July 2009  
93 were analysed for chlorine and bromine content by Dr. A. K. Cheburkin  
94 of the University of Heidelberg using the TITAN-XRF, an energy-dispersive  
95 X-ray fluorescence instrument custom built for the analysis of peat and plant  
96 species (Cheburkin and Shotyk, 2005). Before shipping to Germany in air-  
97 tight zipper-bags the litter and needle material was first washed with de-  
98 ionised water, dried in an oven at 70 °C to constant mass and ground. Limits  
99 of detection were 0.3 and 80 mg kg<sup>-1</sup> for bromine and chlorine, respectively,  
100 with analytical uncertainty estimated to be less than 10 %.

### 101 *3.5. Testing for spatial variability of methyl halide fluxes*

102 At Fir Links (the deciduous forest) normally 3 buckets were filled with  
103 leaf litter from a randomly-chosen position within the forest since it was  
104 not possible to collect leaf litter from the same spot every time. As this  
105 made it impossible to differentiate between temporal and spatial variations  
106 in fluxes, on two occasions fluxes were measured in duplicate from nine points  
107 of a 50 m × 50 m square with sampling points every 25 m in each direction.  
108 Three blank enclosures were also included. The data from these two studies

109 were used to compare spatial with temporal variation of fluxes throughout  
 110 the year.

111 At Griffin Forest five litter samples each were collected from a previously  
 112 thinned, light, relatively dry area and from an un-thinned, dark, relatively  
 113 wet area. Fluxes were calculated against the mean of two parallel blank  
 114 samples.

### 115 3.6. Dependency of fluxes on enclosure time

116 As already stated, fluxes quantified using static enclosure methods may  
 117 vary with length of enclosure time because the accumulation/depletion of  
 118  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  inside the enclosure can alter the behaviour of the rele-  
 119 vant processes. Emissions from leaf litter were highly variable in magnitude  
 120 and often very low. This necessitated long enclosure times to achieve concen-  
 121 trations that were more accurately quantifiable. However, when emissions  
 122 were higher than usual, longer enclosure times may modify fluxes to appear  
 123 smaller per unit time than in the absence of enclosure.

124 To quantify variation in derived flux with enclosure duration, measure-  
 125 ments of a batch of litter were regularly repeated with different enclosure  
 126 times: 6 and/or 24 h at Fir Links; 10 min and 1 h at Griffin Forest. Table 1  
 127 shows the mean ratios of fluxes obtained from those experiments where fluxes  
 128 were derived using two different enclosure durations on a given sample. For  
 129 final comparative interpretation of fluxes at a given site, fluxes were expres-  
 130 sed relative to a common enclosure time of 6 h and 10 min for Fir Links and  
 131 Griffin Forest, respectively, as follows. Fluxes derived from enclosures of the  
 132 duration specified were used without modification. Where flux values at the  
 133 shorter duration were not available for a specific sample or below the limit  
 134 of detection (LOD) they were obtained by multiplying the flux derived from  
 the longer-duration enclosure using the relevant ratio given in the table.

Table 1: Mean ratios of fluxes (and supporting statistical data) obtained from the different enclosure durations specified, for litter material at the two field locations. All correlations shown are statistically significant at  $P < 0.05$ .

Site	$\text{CH}_3\text{Br}$			$\text{CH}_3\text{Cl}$		
	ratio	$R$	$n$	ratio	$R$	$n$
Fir Links, 6 h/24 h	2.40	0.94	28	5.71	0.99	22
Griffin Forest, 10 min/1 h	6.77	0.97	10	2.16	0.95	4

135

136 *3.7. GC analysis*

137 Methyl halide determination by GC-ECD was conducted as described in  
138 Hardacre et al. (2009) and Blei et al. (2010a). Net fluxes were derived from  
139 the difference between sample and blank enclosure values and expressed per  
140 dry litter mass. Uncertainties in individual flux values comprise uncertain-  
141 ties in both instrumental determination of methyl halide concentration in a  
142 gas sample and in the enclosure parameters used to convert concentrations  
143 to flux. The main source of uncertainty derives from interpolation of the  
144 calibration curve. Since both the parallel blank and enclosure samples were  
145 stored and analysed in identical conditions such uncertainties are minimised  
146 by the experimental design of quantification by difference.

147 Discrimination of a significant net flux depends on the ability to determine  
148 significant difference in analyte mixing ratio between an enclosure sample and  
149 parallel blank sample. The LOD for determination of a net flux was thus set  
150 at twice the uncertainty in the associated background sample. The LOD va-  
151 lues vary between individual flux measurements because the uncertainties in  
152 individual sample and background gas analyses, and in estimation of enclosed  
153 volume and foliage mass, vary between measurements. As illustration, the  
154 interquartile ranges of blank fluxes for  $\text{CH}_3\text{Br}$  at Fir Links and Griffin Fo-  
155 rest were estimated to be 0.6 and  $7 \text{ ng kg}^{-1} \text{ h}^{-1}$ , respectively, and for  $\text{CH}_3\text{Cl}$   
156 fluxes, 0.007 and  $0.06 \text{ } \mu\text{g kg}^{-1} \text{ h}^{-1}$  at the two sites, respectively. Negative  
157 fluxes are necessarily semi-quantitative since methyl halide uptake was limi-  
158 ted by the initial concentrations inside the enclosure and any positive flux  
159 from the chamber material itself during the enclosure time.

160 All quoted sd values combine analytical and concentration-to-flux conver-  
161 sion uncertainties, plus, for mean values, the variation between individual  
162 measurements.

163 **4. Results and Discussion**

164 Leaf/needle litter chlorine content was  $<80 \text{ } \mu\text{g g}^{-1}$  dry wt at both sites  
165 whilst mean bromine content was 11.5 and  $3.5 \text{ } \mu\text{g g}^{-1}$  dry wt at Fir Links  
166 (deciduous) and Griffin Forest (conifereous), respectively. Bromine concen-  
167 tration in the leaf litter was therefore almost three times the concentration in  
168 the needle litter, probably due to the coastal location of Fir Links. The bro-  
169 mine concentration for Fir Links litter was in good agreement with the value  
170 of  $8.75 \text{ } \mu\text{g g}^{-1}$  given by Lee-Taylor and Holland (2000) for fine woody matter  
171 from coastal regions. No information could be found for bromine content

172 of coniferous litter for comparison with the Griffin Forest data. Whilst the  
173  $<80 \mu\text{g g}^{-1}$  concentration for chlorine in this work is low in comparison with  
174 the values of 1100 and 2100  $\mu\text{g g}^{-1}$  for fresh leaves from two *Fagus* species re-  
175 ported by Yassaa et al. (2009), it is more in line with the much lower chlorine  
176 content of  $\sim 126 \mu\text{g g}^{-1}$  dry wt reported by Lobert et al. (1999) for temperate  
177 leaf litter rather than fresh plant material.

#### 178 4.1. *Fir Links (deciduous litter)*

179 Net methyl halide fluxes at the deciduous wood were found to vary stron-  
180 gly with time (Figure 1). Whilst fluxes for most of the year were often  
181 very small and mostly slightly negative (uptake) there were two incidences  
182 of large positive net fluxes (production) during September 2008 and March  
183 2009. Due to their magnitude these fluxes dominated the mean annual flux  
184 although most of the time leaf litter took up methyl halides. This result is  
185 important as it shows that fluxes must be monitored over long periods of  
186 time to gain confidence in the long-term mean direction and magnitude of  
187 fluxes in an ecosystem.

188 It is very likely that elevated fluxes during autumn were due to the fall  
189 of fresh leaf litter from the canopy and the elevated fungal and microbial  
190 decomposition activity at this time of year, known to yield methyl halides  
191 (Watling and Harper, 1998; Lee-Taylor and Holland, 2000). Elevated leaf-  
192 litter  $\text{CH}_3\text{Br}$  fluxes in autumn, declining over winter, were also reported by  
193 Drewer et al. (2008). No substantiated explanation can be offered for the  
194 other event, but it is likely relevant that it coincided with the pronounced  
195 rise in ambient air temperatures at the end of a prolonged winter cold period,  
196 suggesting a ‘kick-start’ in (bio)chemical activity. The mean ( $\pm 1$  sd) annual  
197 fluxes expressed per hour were  $4.1 \pm 3.7 \text{ ng kg}^{-1} \text{ h}^{-1}$  and  $0.98 \pm 0.62 \mu\text{g kg}^{-1} \text{ h}^{-1}$   
198 for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , respectively.

##### 199 4.1.1. *The relationship between $\text{CH}_3\text{Br}$ and $\text{CH}_3\text{Cl}$ net fluxes*

200 As is readily visible from Figure 1, fluxes of these two gases followed  
201 very similar temporal trends, and the linear correlation between the two was  
202 highly significant ( $R = 0.81$ ,  $P = 0.0002$ ). This is a clear suggestion that net  
203 fluxes are the result of the same process(es).

204 The  $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$  mass ratio of the average net fluxes was  $\sim 240$  which  
205 corresponds to a Cl/Br mass ratio in methyl halide fluxes of  $\sim 200$ . The  
206  $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$  flux mass ratio is therefore an order of magnitude greater  
207 than the mass ratio of the global budgets of the two gases (Montzka et al.,

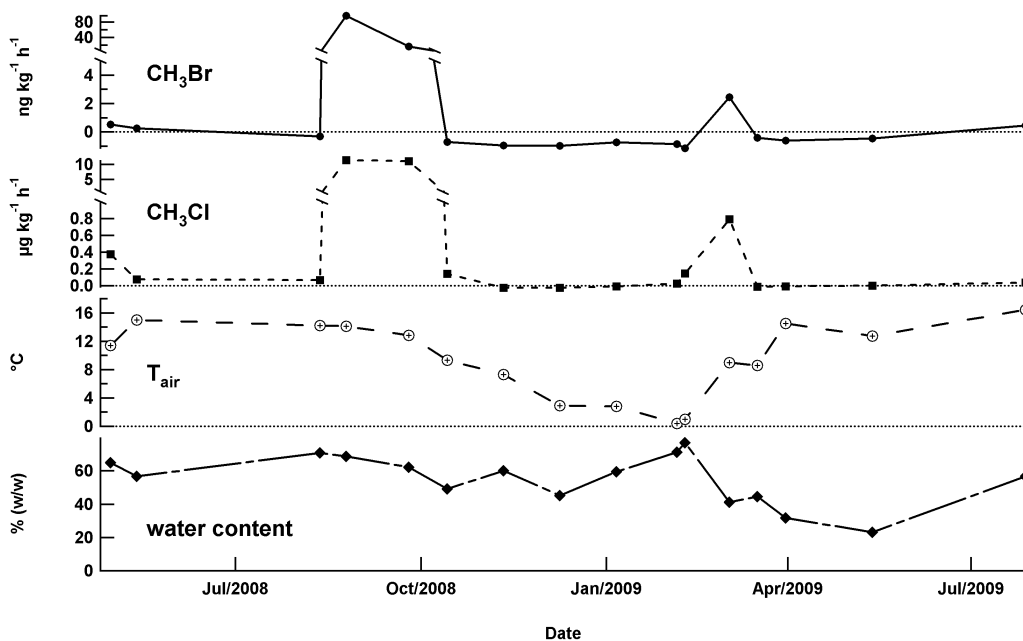


Figure 1: Net  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  fluxes from leaf litter at Fir Links measured from 30<sup>th</sup> April 2008 to 28<sup>th</sup> July 2009 together with mean enclosure temperature and litter gravimetric water content.

208 2002; Clerbaux et al., 2007), indicating that temperate deciduous litter is  
 209 relatively more important as a  $\text{CH}_3\text{Cl}$  source than as a  $\text{CH}_3\text{Br}$  source, as  
 210 was also concluded for tropical vegetation and litter (Blei et al., 2010a). The  
 211  $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$  average emission mass ratio observed here is also broadly si-  
 212 milar to the  $\text{Cl}/\text{Br}$  mass ratio of  $\sim 280$  found in sea water (likely the dominant  
 213 source of halogen in near-coast surface environment). In contrast, findings  
 214 from several studies of salt marsh vegetation show a strong preference for  
 215  $\text{CH}_3\text{Br}$  over  $\text{CH}_3\text{Cl}$  net emission (Rhew et al., 2000; Dimmer et al., 2001;  
 216 Cox et al., 2004; Drewer et al., 2006; Manley et al., 2006; Blei et al., 2010b),  
 217 but the latter are living halophytes, not decaying litter, so differences are not  
 218 unexpected and presumably reflect different underlying causal processes for  
 219 emissions.

#### 220 4.1.2. Spatial vs. temporal variations in methyl halide fluxes

221 The two detailed studies involving 9 sample pairs each on the 9<sup>th</sup> February  
 222 and 28<sup>th</sup> July 2009 revealed that net fluxes for both gases varied spatially  
 223 significantly less than they did over time (one-tailed  $F$ -test at  $P < 0.05$ ). Al-



224 though not direct proof, this evidence and the fact that fluxes during autumn  
225 were orders of magnitudes larger than during the rest of the year, indicates  
226 that spatial flux variations were negligible compared to temporal variations.  
227 This supports the sampling strategy of taking samples from varying locations  
228 on each sampling occasion.

#### 229 *4.1.3. Statistical analysis of possible drivers*

230 Statistical analysis (two-tailed  $t$ -test at  $P < 0.05$ ) did not reveal any  
231 significant correlation between net methyl halide fluxes and ambient air tem-  
232 perature (up to 16 °C) or leaf litter water content over the monitoring period.  
233 This is consistent with previous findings from a study, also with bulk litter, in  
234 the tropical rainforest of Borneo (Blei et al., 2010a) but different to the two  
235 laboratory studies by Hamilton et al. (2003) and Wishkerman et al. (2008)  
236 which showed correlation with temperatures over the (non-overlapping) hi-  
237 gher temperature range of 25–35 °C.

#### 238 *4.1.4. Comparison with previous studies*

239 Only two previous studies have been carried out on methyl halide emis-  
240 sions from in situ leaf litter. The first, by Drewer et al. (2008), at the  
241 Hermitage of Braid woodland site in southern Edinburgh, Scotland, exami-  
242 ned CH<sub>3</sub>Br fluxes only and found mean ( $\pm$ sd) net emission from temperate  
243 deciduous leaf litter of  $43 \pm 33$  ng kg<sup>-1</sup> h<sup>-1</sup>, an order of magnitude larger than  
244 reported here. Aside from the different woodland sites studied, the earlier  
245 measurements spanned only autumn and winter, rather than the full year of  
246 the current study, so the elevated emissions during autumn would upwardly  
247 bias the derived average. Also, Drewer et al. enclosed litter samples for a few  
248 minutes only, therefore minimising any effect of prolonged enclosure times,  
249 whilst samples in this study were enclosed for longer, therefore maximising  
250 precision but potentially at a cost of accuracy. A further issue is that Drewer  
251 et al. (2008), did not directly account for blank effects but checked for blank  
252 fluxes only once at the beginning of their study. This may have led to an  
253 overestimation of net fluxes since fluxes in general were very low and very  
254 often small emissions were observed from the blank enclosures themselves.  
255 Since Drewer et al. used the same enclosures used in this study it is likely  
256 that the blank effect observed here also applies to their study as well. Ul-  
257 timately, however, it is not possible to determine the exact reason for the  
258 apparent difference between the two studies. The mean litter fluxes measu-  
259 red in Borneo by our group were  $1.4 \pm 0.7$  ng kg<sup>-1</sup> h<sup>-1</sup> and  $2.3 \pm 1.0$  µg kg<sup>-1</sup> h<sup>-1</sup>

260 for CH<sub>3</sub>Br and CH<sub>3</sub>Cl, respectively (Blei et al., 2010a). These values are of  
261 similar magnitude to those presented here. Furthermore, the ratio of mean  
262 CH<sub>3</sub>Cl to CH<sub>3</sub>Br emissions of  $\sim 1600$  found in Borneo also indicated that  
263 tropical leaf litter is relatively more important as a CH<sub>3</sub>Cl source than as a  
264 CH<sub>3</sub>Br source, similar to this study. However, it is again stressed that uptake  
265 rates might be underestimated so average fluxes presented here have to be  
266 regarded as upper limits.

#### 267 4.2. Griffin Forest (coniferous litter)

268 Mean ( $\pm 1$  sd) net CH<sub>3</sub>Br and CH<sub>3</sub>Cl fluxes from needle litter were  $5.7 \pm 6.3$   
269  $\text{ng kg}^{-1} \text{h}^{-1}$  and  $0.47 \pm 0.14 \mu\text{g kg}^{-1} \text{h}^{-1}$ , respectively. There was a signifi-  
270 cant difference (two-tailed *t*-test) in gravimetric water content between the  
271 samples in the thinned and un-thinned sections of the forest at  $P \approx 6 \times 10^{-6}$   
272 with mean values of 36 % and 57 %, respectively. However, there was no  
273 significant difference between net methyl halide fluxes from these two sec-  
274 tions at  $P < 0.05$ . This again indicates that water content does not influence  
275 methyl halide emissions from natural litter material for the ambient tempera-  
276 tures experienced in this study (up to 16 °C). Although mean methyl halide  
277 fluxes at Fir Links and Griffin Forest were similar it seems from previously  
278 reported measurements (Drewer et al., 2008) and preliminary studies for this  
279 work that needle litter is more often an emitter than is the case for leaf litter.  
280 As with the discussion above (Section 4.1.4.) on deciduous litter data, Dre-  
281 wer et al. (2008) reported net emissions from needle litter (at Griffin Forest)  
282 about an order of magnitude larger than fluxes found in this study and the  
283 same reasons for this discrepancy likely apply.

#### 284 4.3. Tentative scale-up of litter fluxes and global implications

285 Assuming the data from Fir Links and Griffin Forest are representative  
286 of temperate deciduous and coniferous forests worldwide a very crude scale  
287 up is derived by multiplying the data from the two sites with the areas  
288 for deciduous and coniferous forest and woodland globally of  $15.8 \times 10^{12} \text{m}^2$   
289 and  $12.1 \times 10^{12} \text{m}^2$ , respectively, and estimated litter pools (UNESCO, 1973;  
290 Matthews, 1997). The resulting fluxes are 0.6 % and 5 %, respectively, of the  
291 current estimated CH<sub>3</sub>Br and CH<sub>3</sub>Cl global annual turnovers of  $200 \text{Ggyr}^{-1}$   
292 and  $4400 \text{Ggyr}^{-1}$  (Montzka et al., 2002; Clerbaux et al., 2007). Therefore  
293 nonwoody leaf and needle litter from temperate forests is unlikely to be  
294 important for the global CH<sub>3</sub>Br budget but possibly a moderate source for  
295 the CH<sub>3</sub>Cl budget. Similar conclusions have been noted for vegetation and

296 litter in tropical forests (Blei et al., 2010a). Given the strong variability of  
297 fluxes over time and the lack of understanding of what is ultimately driving  
298 uptake and emission processes of methyl halides from leaf and needle litter  
299 a more precise quantification is avoided. However, it should be noted the  
300 above statements relate to the nonwoody proportion of forest litter, which  
301 was taken to be 30 % of total litter mass (Matthews, 1997); decomposition  
302 of the 70 % coarse woody detritus mass will likely also contribute flux.

## 303 5. Conclusions

304 This study has reported the first measurements of  $\text{CH}_3\text{Cl}$  fluxes from  
305 temperate forest nonwoody leaf litter. Long-term average fluxes were found  
306 to be of the order of  $0.1 \mu\text{g kg}^{-1} \text{h}^{-1}$ . Considering the large area of temperate  
307 forests this makes leaf litter a potentially important source of  $\text{CH}_3\text{Cl}$  globally.

308 Observed  $\text{CH}_3\text{Br}$  fluxes, augmenting measurements already available, were  
309 two orders of magnitude smaller than  $\text{CH}_3\text{Cl}$  fluxes, making nonwoody leaf  
310 litter unlikely to be an important  $\text{CH}_3\text{Br}$  source globally, although previous  
311 measurements on  $\text{CH}_3\text{Br}$  have suggested that fluxes in temperate forests may  
312 be an order of magnitude larger than observed here. Furthermore, no coarse  
313 woody detritus or live plants such as trees were included in this study, ad-  
314 ding further potential to the importance of temperate forests to global methyl  
315 halide budgets.

316 Fluxes from deciduous leaf litter were shown to vary significantly more  
317 over the duration of a year compared with spatial variability. However, on  
318 average, net fluxes for a given methyl halide were comparable between de-  
319 ciduous and coniferous litter. In general the  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  fluxes were  
320 temporally well correlated. The  $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$  mass ratio derived from the  
321 mean flux values of all litter samples was  $\sim 200$ , about 10 times larger than  
322 the ratio derived from global turnover estimates. Future studies should in-  
323 vestigate the extent to which in situ fluxes from leaf and needle litter are the  
324 product of abiotic chemical reactions or microbial/fungal activity.

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