Atmospheric Environment 45 (2011) 1543–1547

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Methyl bromide and methyl chloride fluxes from temperate forest litter

Emanuel Blei [a,b], Mathew R. Heal [a,*]

[a] School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, EH9 3JJ Edinburgh, UK
[b] School of GeoSciences, University of Edinburgh, Crew Building, West Mains Road, EH9 3JN Edinburgh, UK

ARTICLE INFO

Article history:
Received 19 August 2010
Received in revised form
2 December 2010
Accepted 20 December 2010

Keywords:
Methyl halides
Leaf litter
Temperate
Forest

ABSTRACT

Methyl halide fluxes were measured from fine (nonwoody) litter samples at a temperate deciduous forest site in Scotland on 16 occasions over more than a year and at a coniferous forest site. The resulting mean ($\pm$1 sd) CH_3Br and CH_3Cl fluxes were 4.1 $\pm$ 3.7 ng kg^{-1} h^{-1} and 0.98 $\pm$ 0.62 μg kg^{-1} h^{-1}, respectively, for dry mass leaf litter and 5.7 $\pm$ 6.3 ng kg^{-1} h^{-1} and 0.47 $\pm$ 0.14 μg kg^{-1} 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 CH_3Cl/CH_3Br mass ratio of fluxes was ~200 (to 1 sig. fig.), an order of magnitude larger than the ratio of their estimated global turnovers. Temperate forest litter may be a moderate net source of CH_3Cl globally but a negligible source of CH_3Br. These statements refer to the nonwoody litter component only.

1. Introduction

During the last few years a persistent shortfall in estimates of known sources against known sinks of global CH_3Br and CH_3Cl 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 two methyl halide gases are the main natural vectors of bromine and chlorine into the stratosphere, where they account for 37% and 16% of bromine and chlorine related ozone loss, respectively (Fahey, 2007).

Amongst many others, leaf litter has been proposed as a potential globally important source of CH_3Br and CH_3Cl (Watling and Harper 1998; Lee-Taylor and Holland, 2000; Hamilton et al., 2003; Drewer et al., 2008; Wishkerman et al., 2008) but has not been widely studied. This study was therefore established to examine the potential impact of leaf litter from temperate forests on global methyl halide budgets.

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

Of these four forest components (plants, soils, litter and fungi) this study concentrates on small nonwoody detritus (leaves and needles). The reason for this interest is that even small fluxes per unit mass could result in sizeable global fluxes when considering the large extent of temperate forest cover. Moreover, there are to date no field data on CH_3Cl fluxes from temperate forest litter although it has been shown to be a potentially important source of CH_3Br by our group (Drewer et al., 2008), from measurements made during autumn and winter. Another study by our group in Borneo, SE Asia, estimated that CH_3Br and CH_3Cl net flux from tropical forest leaf litter could account for ~0.1% and ~7% of the respective global budgets (Blei et al., 2010a). It is also of interest to examine if any potential source is seasonal to improve information for extrapolation to global budgets.

Two laboratory studies examining the possibility of abiotic production of methyl halides by Hamilton et al. (2003) and Wishkerman et al. (2008) reported that CH_3Cl and CH_3Br fluxes negatively correlate with leaf litter water content and this was also investigated in this work.

2. Field locations

The main field location was Fir Links forest, a 2.05 ha mixed beech (*Fagus sylvatica*) and sycamore (*Acer pseudoplatanus*) woodland planted in 1954, situated adjacent to the North Sea

* Corresponding author.
E-mail address: m.heal@ed.ac.uk (M.R. Heal).

1352-2310/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2010.12.044

coastline within the John Muir Country Park, East Lothian, Scotland (56°0.1′N 002°35.7′W). The site is not cleared of smaller debris and has a perennial layer of leaf litter. During the study, ground vegetation was either sparse or absent and consisted of ferns of varying density. Topographically the site had very few features, being situated on a plateau a few metres above sea level. 124 enclosures on 76 samples were taken on 16 occasions starting on the 30th April 2008 until the 28th July 2009.

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

3. Methodology

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

3.1. Enclosures

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

Depending on the density of the litter layer on the ground, each sample represented a few square metres of forest floor litter. The number of buckets employed for a measurement ranged from 2 to 18 at any time. Except for measurements at Fir Links on the 30th April 2008, fluxes were measured against a blank enclosure. A small temperature data logger monitored the temperature inside a blank bucket during enclosures.

3.2. Determination of fresh mass, dry mass and water content

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

3.3. Correction for litter volumes in enclosures

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

3.4. Bromine and chlorine content of plant material

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

3.5. Testing for spatial variability of methyl halide fluxes

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

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

3.6. Dependency of fluxes on enclosure time

As already stated, fluxes quantified using static enclosure methods may vary with length of enclosure time because the accumulation/depletion of CH_3Br and CH_3Cl inside the enclosure can alter the behaviour of the relevant processes. Emissions from leaf litter were highly variable in magnitude and often very low. This necessitated long enclosure times to achieve concentrations that were more accurately quantifiable. However, when emissions were higher than usual, longer enclosure times may modify fluxes to appear smaller per unit time than in the absence of enclosure.

To quantify variation in derived flux with enclosure duration, measurements of a batch of litter were regularly repeated with different enclosure times: 6 and/or 24 h at Fir Links; 10 min and 1 h at Griffin Forest. Table 1 shows the mean ratios of fluxes obtained from those experiments where fluxes were derived using two different enclosure durations on a given sample. For final comparative interpretation of fluxes at a given site, fluxes were expressed relative to a common enclosure time of 6 h and 10 min for Fir Links and Griffin Forest, respectively, as follows. Fluxes derived from enclosures of the duration specified were used without modification. Where flux values at the shorter duration were not available for a specific sample or below the limit of detection 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	CH_3Br			CH_3Cl		
	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