JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. D7, PAGES 8857-8864, APRIL 16, 2000

Litter decomposition as a potential natural source of methyl bromide

J. M. Lee-Taylor and E. A. Holland[1]

National Center for Atmospheric Research, Boulder, Colorado

Abstract. We assessed the potential significance of global litter decay as a new source of atmospheric methyl bromide. We combined information on the global distribution and quantity of litter decay, litter bromine content, and the halogen-methylating ability of wood-rotting fungi to produce a spatially explicit estimate of CH_3Br emission from litter decay. The uncertainties are large and the potential methyl bromide source varies greatly in response to assumptions made, including those regarding the efficiency of bromine utilization and release. Our best estimate of the potential flux from woody litter, 0.5 - 5.2 kT yr^{-1}, is unable to account for the entire "missing source." Additional possible fluxes from regions of inadequate data and from nonwoody litter may raise this total. This proposed decomposition source is of potential interest to budget calculations and should be experimentally characterized and quantified.

1. Introduction

Methyl bromide (CH_3Br), an agricultural fumigant biocide, is to be phased out of production due to its role in stratospheric ozone depletion [*United Nations Environment Program*, 1997]. CH_3Br has a complex biogeochemical cycle, which is not well understood in detail; present estimates of the global budget are out of balance, with sinks outweighing sources by a factor of 1.5, a quantity of ~83 kT yr^{-1} (1 kT = 1 Gg) [*e.g., Butler and Rodriguez*, 1996; *Kurylo et al.*, 1999]. Characterization of the missing source or sources offers perspective on the relative importance of agro-industrial and natural contributions to the atmospheric bromine burden.

A recent three-dimensional model study [*Lee-Taylor et al.*, 1998] suggests that a CH_3Br budget with an added terrestrial source biased toward tropical and southern hemisphere regions is consistent with remote atmospheric observations. Biogenic trace gases, including nonmethane hydrocarbons, CO_2, NO, CH_4, and N_2O all show greatest emissions in the tropics [*Guenther et al.*, 1995; *Randerson et al.*, 1997; *Müller*, 1992; *Fung et al.*, 1991; *Potter et al.*, 1996]; this suggests that the new CH_3Br source may also be biogenic. Various processes involving plants and CH_3Br are currently indicated but not well quantified globally. Bromine is found in herbaceous vegetables [*Haller et al.*, 1976; *Stärk et al.*, 1971] and is enhanced in plant biomass for at least two sequential crops after CH_3Br soil fumigation [*Ellis et al.*, 1995]. Rapid uptake of atmospheric CH_3Br by green plants, observed by *Jeffers et al.* [1998], was attributed to enzyme activity. Conversely, *Saini et al.* [1995] find enzymatic production of methyl halides, including CH_3Br, from leaf discs when excess halide ion is present, and *Gan et al.* [1998] observe that live *Brassica* plants can convert soil Br^- into gaseous CH_3Br. *Jeffers et al.* [1998] suggest that plants may be either a net source or a net sink for CH_3Br, depending on the ratio of local atmospheric CH_3Br to plant Br^-.

Some fungi release brominated compounds, possibly as by-products of their physiological use of analogous chlorinated compounds [*Hjelm et al.*, 1996]. The production of CH_3Cl by fungi, for use in internal biochemical processes, is descibed by *Watling and Harper* [1998] (henceforth WH98). The methyl halide is released to the atmosphere only in later stages of fungal growth and only by certain groups of fungi. Both CH_3Cl and CH_3Br are readily evolved by the wood-inhabiting fungus *Phellinus tuberculosus* (also known as *Phellinus/Fomes pomaceus*). This fungus methylates halides preferentially in the order I^-, Br^-, Cl^- [*Harper and Kennedy*, 1986]. It is possible that other fungi which release CH_3Cl may also evolve CH_3Br, if Br^- is available.

The genus *Phellinus* is a subdivision (subset) of the family Hymenochaetaceae. Hymenochaetaceous fungi, known colloquially as white rot fungi, colonize wood and wood litter. They are, in turn, classified within the Basidiomycota order of fungi which includes most mushroom-shaped fungi. An investigation of 37 fungus species in the genus *Phellinus* [*Harper et al.*, 1988] showed that the majority have halomethane-emitting capabilities. Some other Hymenochaetaceous genera, such as *Inonotus*, also contained species which produced CH_3Cl, albeit less strongly than did the *Phellinus* species; these genera all had poroid (spongy underside) characteristics in common. *Harper et al.* [1988] found only two isolated cases of CH_3Cl release in fungi of families other than the Hymenochaetaceae and concluded that while the trait is widespread among poroid members of the Hymenochaetaceae, it is confined to that family.

In this paper we explore the potential CH_3Br source due to the decomposition of litter by wood-rotting fungi. Required for this calculation are fungal rates of halide conversion [*Harper et al.*, 1988], the Br^- content of litter [*McKenzie et al.*, 1996; *Slocum et al.* 1979], vegetation distributions

---

[1] Now at Max Planck Institute for Biogeochemistry, Jena, Germany.

Paper number 1999JD901112.
0148-0227/00/1999JD901112$09.00

[*Matthews,* 1983; *Cramer et al.*, 1995], and litter decomposition rates [*Matthews,* 1997; *Schimel et al.*, 1996]. Section 2 gives details of the derivation of each of these quantites and lists assumptions inherent in their use. Section 3 presents the range of resulting estimates for an upper limit to the potential source. We also estimate the spatial distribution of the postulated decomposition-related source of CH_3Br and comment on its potential contribution to the global budget.

Table 1. Litter Decay by Litter Fraction

Scenario	Coarse Woody	Fine Woody	Coarse Roots	Nonwoody Litter Above ground	Nonwoody Litter Below ground	Total
			Global Totals; Pg dry matter yr^{-1}			
M1	11	10	-	22	32	75
M2	11	13	-	28	41	94
C	12	5.3	3.4	20	23	60
			Study Regions Only; Pg dry matter yr^{-1}			
M	17.4	7.7	-	16	24	55
M	27.4	8.1	-	17	25	57
C	8.2	4.2	2.5	14	14	40

Values represent present-day totals.

2. Methods and Models

We calculate the potential annual global CH_3 Br flux, F (kT CH_3Br yr^{-1}), owing to fungal decomposition of woody biomass using the following model:

$$F = \sum_{i=1}^{I} \sum_{l=1}^{n} (D_{i,l}\, [\mathrm{Br}^-]_{i,l}\, 10^{-12} f_{\mathrm{nat},\, i}\, k_l\, m_{\mathrm{CH3Br}}/m_{\mathrm{Br}}), \qquad (1)$$

where for each model cell i and litter fraction l, D is the annual preagricultural decomposition rate (kg dry matter yr^{-1}), [Br$^-$] is the content of Br$^-$ (mg kg^{-1} dry matter) in each litter fraction, f_{nat} is the fraction of the grid cell occupied by natural vegetation, k is the net efficiency of conversion by fungi of Br$^-$ in litter to CH_3Br, expressed as a fraction, and m is molar weight. These terms and the assumptions involved in the model are explained in sections 2.1 - 2.3.

2.1. Litter Decomposition

Inventories of litter production are based on spatially limited observations and are extrapolated to the global scale using vegetation classifications and/or climate data. We used here three different litter decay scenarios, involving compilations by different methods of widely varying estimates. The first scenario, M1, (where the "M" refers to values derived from the work of *Matthews* [1997]) was based on a compilation of direct measurements of aboveground litter production including fine litter, dead leaves and grasses, fine woody matter (FWM, generally < 7cm diameter), and coarse woody detritus (CWD). The second scenario, M2, was based on indirect estimates of litter production inferred from measurements of soil respiration. The third scenario, C, was model based and used the Century model of terrestrial ecosystems to estimate global litter production. All of the scenarios made the steady state assumption that the annual litter production rate equals the annual decomposition rate (D). Table 1 gives global decay totals for each litter fraction in each of the different scenarios, and litter decay totals for the regions considered in this paper. We quote present-day values unless otherwise noted.

Our first two litter decay scenarios were based on different subsets of *Matthews*' [1997] one estimate of coarse litter (CWD) production and nine different estimates of fine litter production. The fine litter production estimates had a preagricultural range of 29 - 139 Pg dry matter yr^{-1} (1 Pg = 10^{15}g), 30 - 35% of which was classified as FWM, based on measurements. The nine fine litter estimates differed in their use of available measurements, methodologies employed (including whether belowground decomposition was included), and extrapolation technique. We included in our calculation the three fine litter production estimates that were most closely related to measured quantities. In each case, production was distributed globally according to biome type [*Matthews*, 1983].

Our Scenario M1 included both *Matthews*' [1997] CWD production and "fine litter case 1". CWD production was compiled from measurements of aboveground live wood and tree mortality rates resulting in an estimate of global aboveground CWD production of 11 Pg dry matter yr^{-1}. Fine litter case 1 was a global compilation of direct measurements of aboveground fine litter production, totaling 32 Pg dry matter yr^{-1}, of which FWM accounted for 10 Pg dry matter yr^{-1}. We accounted for belowground decay by assuming that decay of belowground litter equals aboveground fine litter production [*Matthews,* 1997].

Our second scenario, M2, combined the mean of *Matthews*' [1997] "fine litter cases 3 and 5" with CWD production. In fine litter cases 3 and 5, *Matthews* [1997] inferred fine litter decomposition from measurements of CO_2 evolution [*Raich and Schlesinger* 1992] by assuming that total CO_2 evolution minus respiration by living roots was equal to the sum of above and belowground litter decomposition. The calculation was thus sensitive to root respiration which varied between 20 and 50% of total CO_2 evolution. Cases 3 and 5 differed in the way litter decomposition was extrapolated: Case 3 used the Matthews [1983] defined vegetation classes, while case 5 used the CO_2 evolution/climate relationships developed by *Raich and Schlesinger* [1992]. Global fine litter yields for cases 3 and 5 were 79 and 84 Pg dry matter yr^{-1}, respectively, for a present-day mean of 82 Pg dry matter yr^{-1}, of which 41 Pg dry matter yr^{-1} is assumed to be belowground litter production and 13 Pg dry matter yr^{-1} is FWM (30-35% of the aboveground fraction [*Matthews,* 1997]).

The third litter decay scenario, C, was based on the Century terrestrial ecosystem model [*Schimel et al.* 1996; *Parton et al.*, 1987, 1988, 1993]. The distinguishing feature of Century which made it appropriate for this analysis was the explicit partitioning of live and dead biomass defined by different turnover times. (The model treats leaves, fine roots, coarse roots, branches, and stems as separate components of the total biomass.) By contrast with regression based estimates of litter production [*Rosenzwieg* 1968; *Leith* 1975; *Esser* 1982; *Meetenmeyer et al.* 1982; *Lonsdale* 1988], Century incorporates hydrologic, climatic, and nutrient regulation of both litter production and decomposition [*Schimel et al.*, 1997]. We analyzed results from a global state simulation with preindustrial levels of N deposition and integrated using global climatology, soils, and vegetation descriptions [*Schimel et al.*, 1996]. The 0.5° resolution global simulation was carried out according to the protocols of the Potsdam Intercomparison of the International Geosphere-Biosphere Programme (IGBP) Global Analysis, Interpretation and Modeling Task Force [*Cramer et al.*, 1995]. The following fluxes were integrated to estimate litter decomposition: aboveground grass, belowground grass, leaf, fine root, fine branch, large wood, and coarse root carbon production. Again, we assumed steady state so that litter decomposition was equal to litter production. The net global present-day total was 60 Pg dry matter yr^{-1}, of which 17.7 Pg dry matter yr^{-1} was due to decay of aboveground wood.

2.2. Litter Br^- Content and Distribution

Little information was available on the Br^- content of wood, [Br^-]. *Bowen* [1979] attributed Br^- concentations in wood to *Neufeld* [1936] and *Stella et al.* [1977], who actually analyzed only leaf and fruit materials. *McKenzie et al.* [1996] found that Oregon Douglas fir wood contained no Br^- above their detection limit, while Br^- in litter and soil and on tree surfaces decreased exponentially with distance from the ocean, implying a seasalt deposition source. Br^- was, however, found in measurable quantities in inland litter and vegetation, including wood, in a Brazilian tropical forest and in Zambian savanna [*McKenzie et al.*, 1996]. The only reported analyses of Br^- in wood of temperate deciduous forests were the oak and hickory wood analyses of *Slocum et al* [1979].

Table 2 details the Br^- values assigned to each litter type in each general biome type for which information is available (tropical forest, wooded savanna, temperate deciduous forest, and coastal regions). We assumed that Br^- would be found at similar concentrations throughout a given vegetation type, globally, and that the Oregon coastal measurements of *McKenzie et al.* [1996] could be extended to coasts worldwide. We also assumed that where a Br^- content was recorded for litter in general, that concentration was also appropriate for fine woody matter and for subsurface organic matter. The latter assumption was supported by the observation that the Br^- contents of duff (partially decayed litter) and litter in Oregon are similar [*McKenzie et al.*, 1996]. These authors did not record duff analyses for their other sampling sites. Where two or more Br^- values were given for one location, we used the mean. For temperate deciduous woodland, we extended the wood values of *Slocom et al.* [1979] also to fine woody matter, because there was no recorded information about fine litter in such locations. Since the coastal Br^- values reported by *McKenzie et al.* [1996] reduce exponentially with increasing distance inland, we assigned fine litter Br^- values due to coastal influence over the first 100 km inland worldwide, at the median of the concentrations reported over that distance, unless the local biome type suggested that a higher value was appropriate. *McKenzie et al.* [1996] found no evidence of Br^- in large wood at their Oregon coastal sampling sites, which suggests that the coastal Br^- enhancement they observed in fine wood was due to deposition on plant surfaces rather than uptake in the plant tissues. Since the ratio of surface area to net biomass is much less for coarse woody detritus than for fine materials, we do not include a coastal enhancement factor for the Br^- content of large wood.

Table 2. Br^- Content Assigned by Litter Type

Biome Type	Litter Type	Br^- Content, mg kg^{-1} dry matter
Tropical forest	CWD, CRT	3.7
	FWM	16
	other litter	16
Wooded savanna	CWD, CRT	2.7
	FWM	3.3
	other litter	3.3
Temperate deciduous forest	CWD, CRT	0.065
	FWM	0.065
	other litter	0
Coast	CWD, CRT	0
	FWM	8.75
	other litter	8.75

We distributed the Br^- values assigned to the different biome types using two separate vegetation classification maps. The vegetation map of *Matthews* [1983] was used for the calculations using litter production estimates derived from *Matthews* [1997], while the Century model has been extensively run using parameterizations based on the Potsdam vegetation map [*Cramer et al.*, 1995]. The Matthews vegetation scheme maps the global preagricultural distribution of vegetation, and the Potsdam vegetation scheme maps the distribution of potential natural vegetation, based on a global climate database [*Leemans and Cramer*, 1991; updated data received from W. Cramer, Potsdam]. Accordingly, the land surface covered and quantity of vegetation and litter represented differ between the two maps. When defining biomes for which to calculate CH_3Br release, we considered both the descriptions and the distributions of the vegetation types, to circumvent the inherent differences between the two maps and ensure as close a match as possible between their active areas. Descriptions of the vegetation classes used in each case are shown in Table 3, with corresponding maps in Figures 1a and 1b. To better approximate present-day vegetation distributions, we used the *Matthews* [1983] map of cultivation areas to exclude agricultural areas from our calculation in each case. Cultivated areas were mapped as those areas which grew annual crops. A comparison of Tables 1a and 1b shows that the selected regions, including coastal areas, account for 60-75% of both global woody litter and net litter decay. For our best estimate we did not extrapolate the estimated flux to temperate/boreal evergreen forests and other biomes for which Br^- data is not available.

2.3. Methyl Bromide Release

In estimating the potential conversion of bromine in decomposing litter to gaseous CH_3Br, and subsequent potential CH_3Br flux, it was necessary to make several assumptions regarding various aspects of the conversion and release processes. Our approach was based on that used for CH_3Cl by WH98 and *Khalil et al.* [1999] (henceforth K99). This section deals with the assumptions made and the treatment of associated uncertainties.

Table 3. Inland Biomes Considered in This Study

Biome Type	Class Number	Description
Tropical forest	M:1	tropical evergreen forest, mangrove
	P:16	tropical evergreen forest
Wooded savanna	M:23	tall/medium/short grassland, 10-40% tree cover
	M:24	tall/medium/short grassland, <40% tree cover
	M:25	tall/medium/short grassland, shrub cover
	P:14	tropical savanna
	P:15	arid shrubland
Temperate deciduous forest	M:10	cold deciduous forest, with evergreens
	M:11	cold deciduous forest, no evergreens
	M:16	cold deciduous woodland
	P:8	temperate mixed forest
	P:10	temperate deciduous forest
	P:11	temperate forested wetland

M, vegetation classification by *Matthews* [1983]; P, vegetation distributions from *Cramer et al.* [1995].

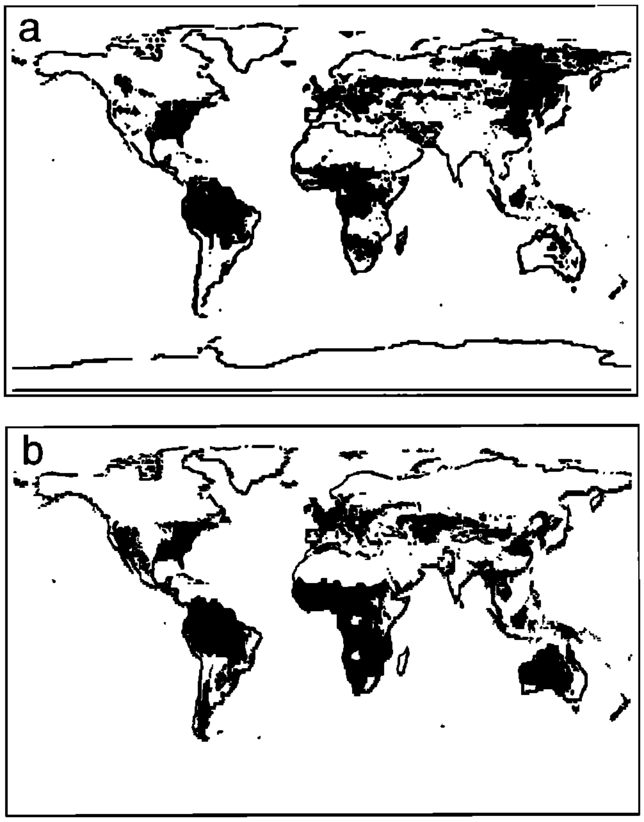

Figure 1. Distribution of regions considered in this study using decay parameters and vegetation distributions from (a) *Matthews* [1983, 1997] and (b) Century [*Schimel et al.* 1996; *Parton et al.* 1987, 1988, 1993; *Cramer et al.* 1995]. White areas represent those biomes for which data on the Br^- content of vegetation are not available.

The first main assumption was that poroid hymenochaetaceous fungi behave in the natural environment as they do under laboratory conditions, with respect to halide methylation and release. *Phellinus tuberculosus*, the only fungus culture for which Br^- methylation has been investigated, released CH_3Br at 70% efficiency, slightly lower than its CH_3Cl release efficiency [*Harper and Kennedy*, 1986]. We therefore assumed, for all estimates, that all species of fungi would show equal release efficiencies for CH_3Cl and CH_3Br. Apart from an inhibition of methylation at high, presumably toxic, Br^- concentrations, the conversion efficiency shown by *P. tuberculosus* was independent of Br^- concentration [*Harper and Kennedy*, 1986]. We assumed in addition, in the absence of any information to the contrary, that neither temperature nor moisture would affect the efficiency of halide conversion (though the rate of litter decay may well be affected).

Fungal decay is the main pathway by which woody litter is decomposed [*Cooke and Rayner*, 1984; WH98]. However, a small proportion of the decomposition occurs via the action of ants and other insects, during wood burning, or under waterlogged conditions, and is therefore not involved in fungally mediated methyl halide emissions. This was accounted for by factor *A* (Table 4 and (2) [WH98 and K99]), the proportion of woody decomposition due to polypore fungi, which varies in different geographical regions. Considering that the hyphae of wood-inhabiting fungi may easily penetrate well into nonwoody litter [WH98] made a much larger pool of trace elements potentially available for uptake and processing by fungi. This issue was not considered in the quantification of uncertainties associated with the potential flux of CH_3Br from woody litter. We therefore made an additional set of estimates, assuming that nonwoody litter (including surface soil litter) was also available for fungal colonization, in order to assess the upper limits to the CH_3Br flux, should this process be important. The flux estimate involving only woody litter should be regarded as the best estimate and is directly comparable with the estimate of CH_3Cl flux made by WH98 and K99.

The hymenochaetaceous fungi are not the only polypores involved in woody decay. To account for the fact that these other families are not known to emit methyl halides, WH98 and K99 adopted a global mean factor of 20% (factor *H* in Table 4 and (2)), the approximate proportion of the total

Table 4. Factors for Calculation of Fungal Emissions

Factor	Tropics/ Subtropics, %	Temperate Regions, %	Australia, %
A	75	95	85
H	20	20	20
G_P	70	60	70
G_O	30	40	30
E_P	15	15	15
E_O	5	5	5

From *Khalil et al.* [1999].

number of polypore species classified in the family hymenochaetaceae. The assumption was implicit that hymenochaetaceous fungi can colonize woody litter worldwide. This assumption was supported by the fact that *Têtu-Bernier et al.* [1983] listed a wide variety of host wood types for cultures of many of the fungi investigated by *Harper et al.* [1988] and that the review by WH98 showed records of such species from all geographical areas except South America and southeast Asia, for which data are unavailable. It was also implicitly assumed that the relative abundance of individual active fungi was equal to the relative abundance of active species. These assumptions, and the associated uncertainties, were included in the estimation of the range of the potential methyl halide flux. However, the best estimate of the flux did not take account of the fact that most polypore fungus species (around 1220) have not yet been investigated for methyl halide release and may or may not have this ability (K99). This uncertainty represents an unknown quantity, whose possible impact could be to raise the best estimate of net flux by up to a factor of 5, in the unlikely event that all other polypore fungus species have this ability.

The genus *Phellinus* was found by *Harper et al.* [1988] to show significantly greater efficiency of CH_3Cl conversion and release (E) than did other genera of poroid hymenochaetaceous fungi. WH98 and K99 therefore considered the relative numbers of *Phellinus* species, (G_P), and other species, (G_O), in different geographical regions (Table 4). The mean conversion efficiency for CH_3Cl release shown by all 60 species of poroid hymenochaetaceous fungi investigated by *Harper et al.* [1988] was 10%, within a range of 0-30% (± 1 s.d.).

Consideration of the above factors yields the following expression for the net efficiency of conversion by fungi of Br^- in litter to CH_3Br, denoted k in (1) (after WH98 and K99) :

$$k_i = \frac{[A_i\ H\ (G_{P,i}\ E_P + G_{O,i}\ E_O)]}{100}, \tag{2}$$

where, for each model cell, i, A is the proportion of woody decomposition due to polypore fungi, H is the proportion of hymenochaetaceous polypore species, G_P and G_O are the proportion of species from that family in the genus *Phellinus* and in other genera, respectively, and E_P and E_O are the methyl halide release efficiencies of the two genus groups. Table 4 gives a complete listing of the values adopted for these factors, by geographic region.

Quantifiable uncertainties were treated explicitly by K99 to assign a 90% uncertainty range to their calculated global CH_3Cl flux. They quoted a range from 0.27 to 3.0 times the net flux. Since much of the information we used to calculate the potential CH_3Br flux was taken directly from the work of WH98 and K99, we assigned the same error margin to our best estimate of the CH_3Br flux. Although our calculation of the annual woody decay rate relied on different data to that of WH98 and K99, the contribution to the net uncertainty was the same in each case. We could not assign an uncertainty estimate to the concentration of Br^- present in wood, owing to the scarcity of data. The uncertainty treatment by WH98 and K99 did include a term for the Cl^- concentration of wood. Our adoption of the same range in the potential flux assumed that the contribution to the total uncertainty was the same for the two different trace constituents.

3. Results and Discussion

Our best estimate of the potential flux of methyl bromide due to wood-rotting fungi is 0.5-5.2 kT yr^{-1}, with a geometric mean of 1.7 kT yr^{-1}. This value, the mean result from our three litter scenario calculations, represents the potential flux of CH_3Br due to the action of poriod hymenochaetaceous fungi on aboveground woody litter, in the regions under consideration. The results from the different scenarios are in fairly close agreement both in magnitude (Table 5) and in distribution (Plate 1) with fluxes concentrated in the equatorial forested regions. Coastal areas, temperate/cool forests, and wooded grasslands show considerably lower rates of CH_3Br flux from this source. The source distribution is broadly consistent with that required by current models of the so-called "missing source" of CH_3Br [eg., *Lee-Taylor et al*, 1998]. (The distribution map given by scenario M2 is not shown but is very similar to that from M1).

We have indicated three main areas where lack of applicable information has restricted the size of our estimate of the potential CH_3Br flux due to fungal action on decaying vegetation. First, if uninvestigated species of fungi are capable of CH_3Br synthesis and release, the net flux will be larger than the best estimate. Second, if methylation and release of Br^- from litter pools other than woody litter occurs, the net flux will, again, be greater. Table 5 lists estimated maximum fluxes for action by known fungi only, owing to the inclusion of nonwoody litter in the active litter total. It is possible that this litter fraction may make at least some contribution to the net source, though we have not included it in our best estimate of the flux. Belowground CH_3Br emission (Table 5) is, likewise, omitted from the best estimate, owing to the potential for reuptake of the gas by the surrounding soil and/or by soil fauna [*Shorter et al.*, 1995; *Serça et al.*,1998; *Hines et al.*, 1998] and consequent

Table 5. Estimated CH_3Br Flux From Decaying Vegetation, by Litter Fraction

Scenario	Woody Litter, kT yr^{-1} (Best Estimate)	Aboveground Fine Litter, kT yr^{-1}	Belowground, kT yr^{-1}	Net, All Litter, kT yr^{-1}
M1	1.9 (0.5 - 5.7)	4.2	6.2	12.3 (3.3 - 37)
M2	1.8 (0.5 - 5.4)	3.8	5.8	11.4 (3.1 - 34)
C	1.5 (0.45 - 4.5)	4.3	3.4	9.3 (2.5 - 28)

Estimated ranges are in parentheses.

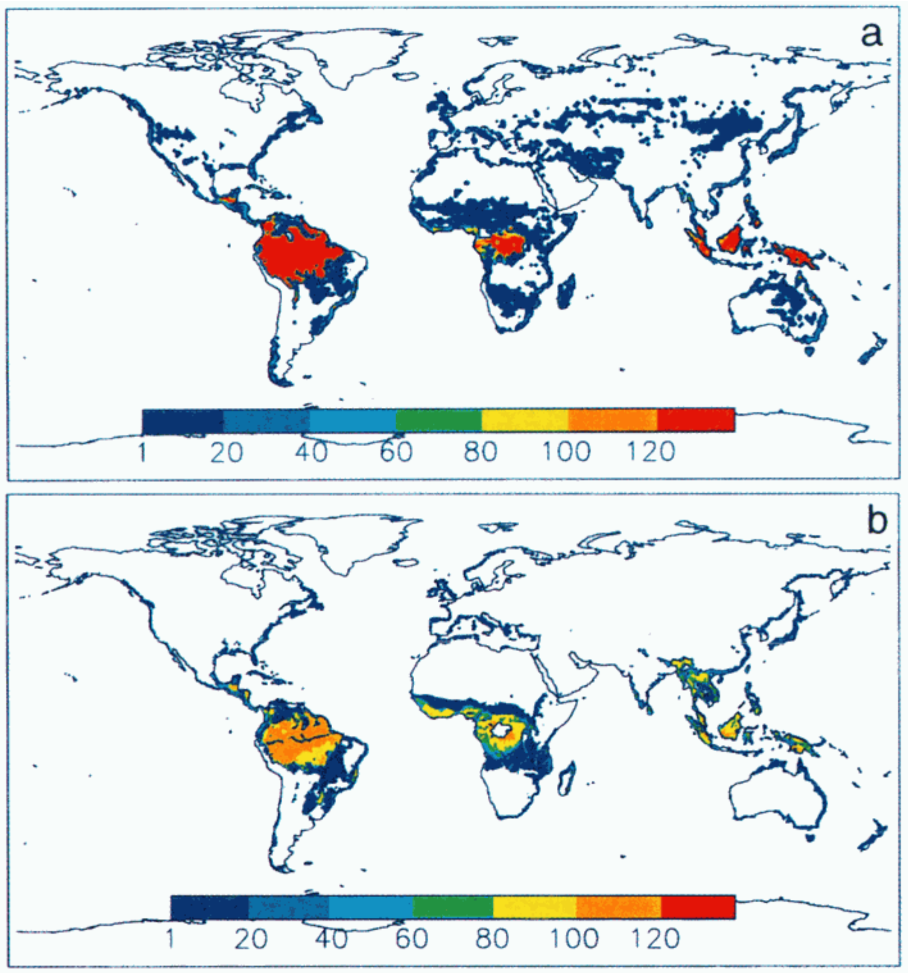

Plate 1. Global distribution of "best estimate" potential CH_3Br flux. Units are g km^{-2} yr^{-1}. (a) Case M1 and (b) Case C are shown.

large uncertainty regarding the potential flux from the belowground litter pool. Third, our best estimate of the flux does not include the 25 -40% of global woody decay for which Br^- data is not available; the estimate is therefore not truly a global flux. Here, again, inclusion of the missing data could possibly increase the estimate of CH_3Br flux.

A CH_3Br flux of 0.5 - 5.2 (1.7) kT yr^{-1} forms only a small fraction of the "missing source," which is about 83 kT yr^{-1} [e.g., *Butler and Rodriguez,* 1996; *Kurylo et al.*, 1999]. Our best flux estimate is similar to the gasoline combustion-related source of CH_3Br, less than 5 kT yr^{-1} [*Baker et al.*, 1998, *Chen et al.*, 1999]. The uncertainties in our estimate, however, are sufficiently large to suggest that a well-constrained assessment of the potential flux of CH_3Br from fungal biosynthesis could be of interest in budget calculations. There are several possible approaches to address the question of this potential source. Any new information regarding the Br^- content of woody litter would be a significant addition to the two literature sources currently available and should be relatively straightforward to obtain. By contrast, the studies of litter decay amounts and distributions quoted here represent the wide-ranging work of many investigators and would be extremely difficult to improve upon. The key issues of uncertainty, however, are the ability of methylating fungi to utilize and convert bromide within litter and the distribution of such activity both globally and within a soil/litter profile. Flux sampling experiments, both in the laboratory and in the field, measuring the rate of CH_3Br flux from the litter surface into the atmosphere would be the ideal means of reducing the uncertainty as to the magnitude of this source.

4. Conclusions

We have used global litter decay inventories and information about methylation of Br^- in decaying vegetation by fungi to assess the plausibility of this route as a source of CH_3Br to the atmosphere. Our best estimate, based on a relatively conservative set of assumptions, indicates a potential flux of 0.5-5.2 (1.7) kT yr^{-1}. The potential flux appears to be concentrated in the equatorial forests. We advise that in situ flux measurements be made to ascertain whether this flux does, in fact, exist and, if so, whether its magnitude is more or less significant than our study suggests.

Acknowledgements. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation. J. M. Lee-Taylor would like to thank E. Atlas, W. H. Taylor, S. Madronich and G. P. Brasseur for logistical support. The assistance of R. McKeown, CSU, in obtaining Century model output was invaluable. The authors are grateful to S. M. Schauffler, P. Harley, and two anonymous reviewers for their encouragement and constructive suggestions.

References

Baker, J. M., C. E. Reeves, S. A. Penkett, and L. M. Cardenas, An estimate of the global emissions of methyl bromide from automobile exhausts, *Geophys. Res. Lett.*, *25*, 2405-2408, 1998.

Bowen, H. J. M., *Environmental Chemistry of the Elements*, Academic, San Diego, Calif., 1979.

Butler, J. H., and J. M. Rodriguez, Methyl bromide in the atmosphere, in *The Methyl Bromide Issue*, edited by C. H. Bell, N. Price, and B. Chakrabarti, ch. 2, pp. 27-90, John Wiley, New York, 1996.

Chen, T. -Y., D. R. Blake, J. P. Lopez, and F. S. Rowland, Estimation if global vehicular methyl bromide emissions: Extrapolation from a case study in Santiago, Chile, *Geophys. Res. Lett.*, *26*, 283-286, 1999.

Cooke, R. C., and A. D. M. Rayner, *Ecology of Saprotrophic Fungi*, pp.196-237, Addison-Wesley-Longman, Reading, Mass., 1984.

Cramer, W., M. Claussen, and A. M. Solomon, An assessment of different climate change scenarios for the global redistribution of agricultural land, paper presented at First Scientific Conference, Global Analysis, Interpretation and Modeling Framework Activity, International Geosphere-Biosphere Programme (IGBP-GAIM), Garmisch-Partenkirchen, Germany, Sept. 25-29, 1995.

Ellis, J. R., D. M. H. Watson, G. E. Varvel, and M. D. Jawson, Methyl bromide soil fumigation alters plant element concentrations, *Soil Sci. Soc. Am. J.*, *59*, 848-852, 1995.

Esser, G., I. Aselmann, and H. Leith, Modeling the carbon reservior in the system compartment "litter," *SCOPE/UNEP Sonderband Heft 52*, pp. 39-58, Geol.-Palaeontol. Inst. Univ. Hamburg, Germany, 1982.

Fung, I., J. John, and J. Lerner, Three dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, *96*, 13,033-13,065, 1991.

Gan, J., S. R. Yates, H. D. Ohr, and J. J. Sims, Production of methyl bromide by terrestrial higher plants, *Geophys. Res. Lett.*, *25*, 3595-3598, 1998.

Guenther, A., et al., A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, *100*, 8873-8892, 1995.

Haller, W. A., L. A. Rancitelli, and J. A. Cooper, Instrumental determination of trace elements in plant tissue by neutron activation analysis and Ge(Li) gamma-ray spectrometry, *J. Agric. Food Chem.*, *16*, 1036ff, 1976.

Harper, D. B., and J. T. Kennedy, Effect of growth conditions on halomethane production by *Phellinus* species: Biological and environmental implications, *J. Gen. Microbiol.*, *132*, 1231-1246, 1986.

Harper, D. B., J. T. Kennedy, and J. T. G. Hamilton, Chloromethane biosynthesis in poroid fungi, *Phytochemistry*, *27*, 3247-3253, 1988.

Hines, M. E., P. M. Crill, and R. C. Harriss, Rapid consumption of low concentrations of methyl bromide by soil bacteria, *Appl. Environ. Microbiol.*, *64*, 1864ff, 1998.

Hjelm, O., H. Borén, and G. Öberg, Analysis of halogenated organic compounds in coniferous forest soil from a *Lepista nuda* (wood blewitt) fairy ring, *Chemosphere*, *32*, 1719-1728, 1996.

Jeffers, P. M., N. L. Wolfe, and V. Nzengung, Green plants: A terrestrial sink for atmospheric CH_3Br, *Geophys. Res. Lett.*, *25*, 43 - 46, 1998.

Khalil, M. A. K., R. M. Moore, D. B. Harper, J. M. Lobert, D. J. Erickson, V. Koropalov, W. T. Sturges, and W. C. Keene, Natural emissions of chlorine-containing gases: Reactive chlorine emissions inventory, *J. Geophys. Res.*, *104*, 8333-8345, 1999.

Kurylo, M. J., et al., Short-lived ozone-related compounds, in *Scientific Assessment of Ozone Depletion: 1998*, rep. 44, ch. 2, World Meterol. Org. Global Ozone Res. and Monit. Proj., Geneva, Switzerland, 1999.

Leemans, R., and W. Cramer, The IIASA database for mean monthly values of temperature, precipitation and cloudiness of a global terrestrial grid, *RR-91-18*, Int. Inst. for Appl. Sys. Anal. (IIASA), Laxenburg, Austria, 1991.

Lee-Taylor, J. M., S. C. Doney, G. P. Brasseur, and J. -F. Müller, A global 3-D coupled atmosphere-ocean model of methyl bromide, *J. Geophys. Res.*, *103*, 16,039-16,059, 1998.

Lieth, H., Primary production of the major vegetation units of the world, in *Primary Productivity of the Biosphere*, edited by H. Lieth, and R. H. Whittaker, pp. 203-215, Springer-Verlag, New York, 1975.

Lonsdale, W. M., Predicting the amount of litterfall in forests of the world, *Ann. Botany*, *61*, 319-324, 1988.

Matthews, E., Global vegetation and land use: New high-resolution databases for climate studies, *J. Clim. Appl. Meterol.*, *22*, 474-486, 1983.

Matthews, E., Global litter production, pools and turnover times: Estimates from measurement data and regression models, *J. Geophys. Res.*, *102*, 18,771-18,800, 1997.

McKenzie, L. M., D. E. Ward, and W. M. Hao, Chlorine and bromine in the biomass of tropical and temperate ecosystems, in *Biomass Burning and Global Change*, edited by J. S. Levine, ch. 23, pp. 241-248, MIT Press, Cambridge, Mass., 1996.

Meetenmeyer, V., E. O. Box, and R. Thompson, World patterns and amounts of terrestrial plant litter production, *BioScience, 32*(2), 125-128, 1982.

Müller, J. -F., Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, *J. Geophys. Res., 97,* 3787-3804, 1992.

Neufeld, A. H., Biochemistry of bromine I, *Can. J. Res. Sect. B, 14B,* 160-194, 1936.

Parton, W. J., D. S. Schimel, C. V. Cole, and D. S. Ojima, Analysis of factors controlling soil organic matter levels in Great Plains grasslands, *Soil Sci. Soc. Am. J., 51,* 1173-1179, 1987.

Parton, W. J., J. W. B. Stewart, and C. V. Cole, Dynamics of C, N, P and S in grassland soils: A model., *Biogeochem. 5,* 109 - 131, 1988.

Parton, W. J., *et al.*, Observations and modeling of biomass and soil organic matter dynamics for the grassland biome worldwide, *Global Biogeochem. Cycles, 7,* 785-809, 1993.

Potter, C. S., P. A. Matson, P. M. Vitousek, and E. A. Davidson, Process modeling of controls on nitrogen trace gas emissions from soils worldwide, *J. Geophys. Res., 101,* 1361-1377, 1996.

Raich, J. W., and W. H. Schlesinger, The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate, *Tellus, Ser. B, 44,* 81-99, 1992

Randerson, J. T., M. V. Thompson, T. J. Conway, I. Y. Fung, and C. B. Field, The contribution of terrestrial sources and sinks to trends in the seasonal cycle of atmospheric carbon dioxide, *Global Biogeochem. Cycles, 11,* 535-560, 1997.

Rosenzwieg, M. L., Net primary productivity of terrestrial communities: Prediction from climatological data, *Am. Nat., 102,* 67-74, 1968.

Saini, H. S., J. M. Attieh, and A. D. Hanson, Biosynthesis of halomethanes and methanethiol by higher plants via a novel methyltransferase reaction, *Plant Cell Environ., 18,* 1027-1033, 1995.

Serça, D., A. Günther, L. Klinger, D. Helmig, D. Hereid, and P. Zimmerman, Methyl bromide deposition to soils, *Atmos Environ., 32,* 1581-1586, 1998.

Schimel, D. S., B. H., Braswell, R. McKeown, D. A. Ojima, W. J. Parton, and W. Pulliam, Climate and nitrogen controls on the geography and timescales of terrestrial biogeochemical cycling, *Global Biogeochem. Cycles. 10*(4), 677-692, 1996.

Shorter, J. H., C. E. Kolb, P. M. Crill, R. A. Kerwin, R. W. Talbot, M. E. Hines, and R. C. Harriss, Rapid degradation of atmospheric methyl bromide in soils, *Nature, 377,* 717-719, 1995.

Slocum, D. H., E. A. McGinnes Jr., and D. M. McKown, Elemental analysis of oak and hickory charcoal using neutron activation analysis, *Wood Fiber, 10,* 200-209, 1979.

Stärk, H., A. Süss, and K. Trojan, *Landwirtsch. Forsh., 24,* 129ff, 1971.

Stella, R., N. Genova, and M. DiCasa, Halogen determination in vegetable NBS standard reference materials - fluorine by isotope dilution - chlorine, bromine , iodine by neutron-activation analysis, *Radiochem. Radioanal. Lett., 30,* 65-74, 1977.

Têtu-Bernier, P., P. J. Maruyama, and Y. Hiratsuka, List of fungal cultures deposited at the Northern Forest Research Centre, 59 pp., inf. rep. *NOR-X-249,* North. For. Res. Cent., Edmonton, Alberta, Canada, 1983.

United Nations Environment Program (UNEP), Report of the ninth meeting of the parties to the Montreal protocol on substances that deplete the ozone layer, UNEP/OzL.Pro.9/12, UNEP, Nairobi, Kenya, 1997. (http://www.unep.org/ozone/9mop-rpt.htm)

Watling, R., and D. B. Harper, Chloromethane production by wood-rotting fungi and an estimate of the global flux to the atmosphere, *Mycol. Res., 102,* 769-787, 1998.

J. M. Lee-Taylor, Atmospheric Chemistry Division, NCAR, 1850 Table Mesa Drive, Boulder, CO 80303. (julial@ucar.edu)

E. A. Holland, Max Planck Institute for Biogeochemistry, Tatzendpromenade 1a, 07745 Jena, Germany.

(Received June 8, 1999; revised November 1, 1999;
accepted November 2, 1999.)