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Production of methyl bromide in a temperate forest soil

Ruth K. Varner
University of New Hampshire, Durham, ruth.varner@unh.edu

Marguerite L. White
University of New Hampshire, Durham

Cindy H. Mosedale
University of New Hampshire, Durham

Patrick M. Crill
Stockholm University

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Production of methyl bromide in a temperate forest soil

Ruth K. Varner, Marguerite L. White, Cindy H. Mosedale, and Patrick M. Crill

Complex Systems Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire, USA

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[1] Field enclosure measurements of a temperate forest soil show net uptake of ambient methyl bromide (CH_3Br), an important trace gas in both tropospheric and stratospheric ozone cycling. The net flux for 1999 was estimated to be -168 ± 72 μg CH_3Br m^{-2} (negative indicates loss from the atmosphere). Individual enclosure flux measurements ranged from -4.0 to $+3.3$ μg CH_3Br m^{-2} d^{-1}. Soil consumption of CH_3Br was estimated from laboratory soil incubations. Production of CH_3Br was calculated as the difference between net flux and predicted consumption. Fungi could be responsible for the production of CH_3Br in this temperate forest soil. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1615 Global Change: Biogeochemical processes (4805); 0330 Atmospheric Composition and Structure: Geochemical cycles; 9350 Information Related to Geographic Region: North America. **Citation:** Varner, R. K., M. L. White, C. H. Mosedale, and P. M. Crill, Production of methyl bromide in a temperate forest soil, *Geophys. Res. Lett.*, *30*(10), 1521, doi:10.1029/2002GL016592, 2003.

1. Introduction

[2] The tropospheric budget of CH_3Br is out of balance with sinks exceeding sources by 59 Gg yr^{-1} [*Yvon-Lewis*, 2000]. Natural sources and sinks are of particular concern because significant gaps remain in our understanding of ecosystem CH_3Br cycling.

[3] Several terrestrial sources of CH_3Br have been identified [*Gan et al.*, 1998; *Varner et al.*, 1999b; *Redeker et al.*, 2000; *Rhew et al.*, 2000; *Dimmer et al.*, 2001; *Rhew et al.*, 2001]. The production mechanism of CH_3Br in these ecosystems is uncertain. Abiotic production of methyl halides can occur during the oxidation of organic matter [*Keppler et al.*, 2000]. Leaf disc studies of a variety of plants, including *Brassica* [*Gan et al.*, 1998], have shown that enzyme mediated methyl transferase can produce CH_3Br [*Attieh et al.*, 1995; *Saini et al.*, 1995]. Wood rotting fungi and ectomycorrhizal fungi are also potential sources of CH_3Br in these ecosystems [*Harper*, 1985; *Lee-Taylor and Holland*, 2000 (L-TH2000); *Redeker et al.*, unpublished (KR2003)].

[4] Consumption and production of CH_3Br may be occurring simultaneously in these ecosystems. *Jeffers et al.* [1998] report a variety of leaves consume elevated levels of CH_3Br. Soil has also been identified as a sink of atmospheric CH_3Br [*Shorter et al.*, 1995; *Serça et al.*, 1998]. *Hines et al.* [1998] determined the process to be aerobic bacterial uptake. Bacteria that consume fumigant and ambient levels of CH_3Br have been isolated from soil [e.g., *Connell Hancock et al.*, 1998; *Miller et al.*, 1997; *Goodwin et al.*, 2001].

[5] This paper examines production and consumption of CH_3Br in a temperate forest soil in New Hampshire. Field measurements of soil-atmosphere exchange of ambient CH_3Br were completed from May 28 to October 28, 1999. Rates of CH_3Br consumption in the soil were estimated with a model derived from temperature and moisture manipulated soil incubations. We estimated production in the soil as the difference between measured net flux from field measurements and the modeled consumption based on soil incubations.

2. Methods

2.1. Field Measurements

[6] College Woods (43°08′N, 71°57′W), Durham, NH is a mixed deciduous conifer forest abandoned as a woodlot approximately 110 years ago. Soils are well drained, weakly to moderately acidic inceptisols with a thin, variable litter layer. A dark organic rich layer extended from 0 to 5 cm then transitioned into light brown mineral soil below 5 cm. [*Crill*, 1991].

[7] Field enclosure measurements were made on a near weekly basis from May 28 to September 9 with two additional measurements on September 24 and October 28. Measurements were completed at two aluminum collars previously established at the site in 1989 [*Crill*, 1991]. One was located on the slope of a small hill while the other collar was in a hollow approximately 5 m away. There was no above-ground vegetation in the collars.

[8] An aluminum enclosure (0.152 m^3 volume), with a fan mounted inside to mix the headspace, was placed on the collar and sealed with water. Four headspace samples (2.5L) were collected every 5 minutes. The gas samples were collected in stainless-steel electropolished cylinders and analyzed for CH_3Br by GC-ECD as described in *Kerwin et al.* [1996]. Artifacts due to enclosure configuration were below the analytical limit of detection.

[9] Soil samples of litter, 0–5 cm (organic layer) and 5–10 cm (mineral layer) were collected. Soil moisture was calculated as soil weight loss after oven drying at 75°C for 24 hrs divided by the dry weight of the sample. Air and soil surface, 5 and 10 cm temperatures were measured manually while datalogger recorded hourly-averaged air, 2, 8, and 15 cm soil temperatures from thermistors.

2.2. Laboratory Incubations

[10] Static soil incubations were performed to determine the consumption rate of CH_3Br. Soil samples were collected from College Woods, stored at 4°C in air tight plastic bags

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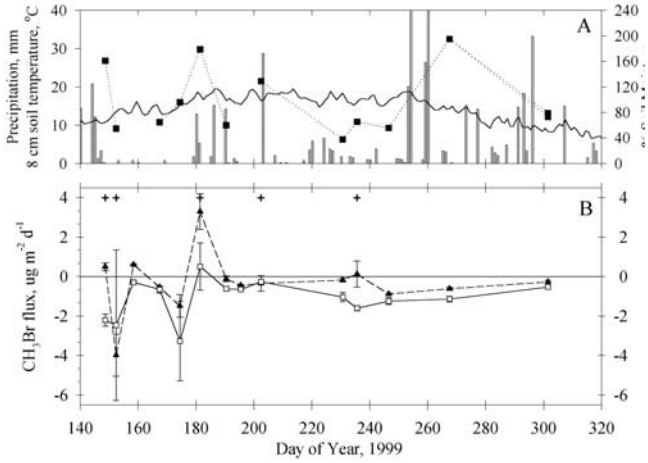

Figure 1. A. Daily total precipitation (bars), hourly average −8 cm soil temperature (solid line) and soil moisture (squares and dotted line) for 1999. B. CH_3Br flux measurements for College Woods for the two collars. Error bars are the error of the linear regression of the concentration versus time flux data. The cross indicates days when Br- ion in the soil was measured.

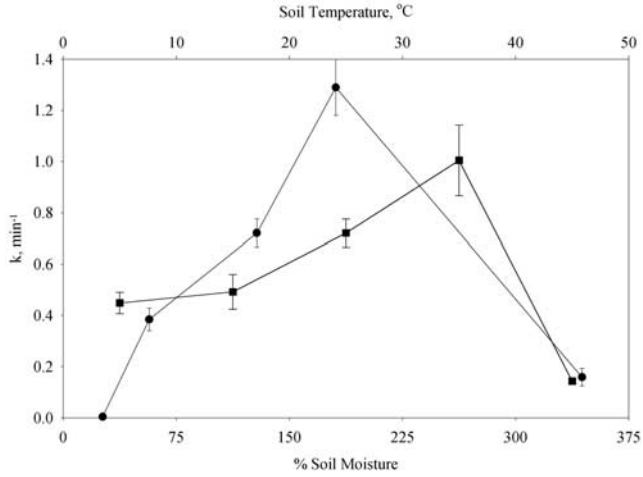

Figure 2. College Woods 0–3 cm soil temperature and moisture manipulations. Uptake rate constant versus %soil moisture content at 25°C (■) and temperature at 128.5% soil moisture (●).

and were processed within 1 week of collection. For more details on the sampling and analysis method see *Kerwin et al.* [1996]. A reaction rate constant, k (min^{-1}), was determined as the slope of the regression fit of the natural log of nmoles of CH_3Br versus time. Uptake rate constants were determined for the soil at 5, 15, 25, 35 and 45°C and for moisture contents ranging from 26.3% to 344%.

3. Results

3.1. Field Measurements

[11] The mean flux for the site was -0.70 ± 0.31 μg CH_3Br m^{-2} d^{-1} (Figure 1B). Seasonal flux was calculated based on a 240 day growing season as -168 ± 72 μg CH_3Br m^{-2}.

3.2. Soil Incubations

[12] By applying a Gaussian fit to the soil incubation data (Figure 2), the predictor equation for k becomes

$$-k = 1.24e^{-0.5\left[\left(\frac{x-26.85}{18.57}\right)^2+\left(\frac{y-194.34}{77.80}\right)^2\right]}. \quad (1)$$

x and y are soil temperature (°C) and soil moisture, respectively. This fit resulted in an $r^2 = 0.853$ and an estimate of error for k of ±0.21 min^{-1}.

[13] The model was then used to estimate field uptake rate constants using soil moisture and temperature data collected during the 1999 sampling season. Soil consumption of CH_3Br for each day of sampling was calculated from *Varner et al.* [1999a]. A production estimate of CH_3Br was calculated for 5 sampling days as the difference between the measured or net flux and the estimated consumption (Table 1).

4. Discussion

4.1. CH_3Br Flux Measurements

[14] These are the first seasonal field measurements of CH_3Br exchange in a temperate forest. The net measurements range from −3.0 to +4.0 μg CH_3Br m^{-2} d^{-1} and overlap the range seen in the more arid shrubland environments in Southern California (−0.95 to + 14.7 μg m^{-2} d^{-1}) [*Rhew et al.*, 2001]. High moisture and organic matter content in the soil could account for higher rates of consumption [*Hines et al.*, 1998]. The soil moisture of the *Rhew et al.* [2001] sites ranged from 0.3 to 24%. We measured a minimum moisture content of 50%. Organic matter content data was not reported for the shrubland study. Our site ranged in organic matter from 78.5% (0 – 5 cm) to 17.4% (5–10 cm).

4.2. Consumption and Production Estimates

[15] Using laboratory-derived rates of consumption in a field setting brings with it many uncertainties. The bulk

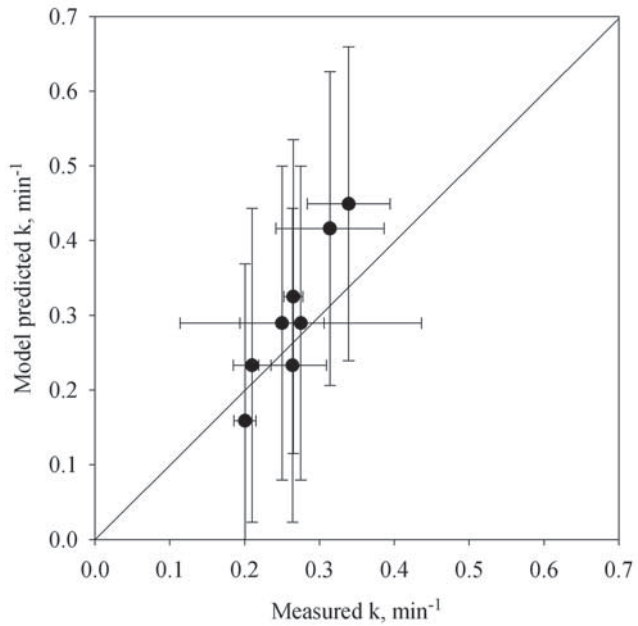

Figure 3. Modeled versus measured consumption of CH_3Br for field data from 1994.

Table 1. Measured Net Flux, Modeled Consumption and Estimated Production of CH_3Br in College Woods Soils

Sampling Date	Surface soil Br^- (mM)	Measured Net Flux	*Modeled Consumption*	*Field Production*	*EF high and low (SD)*	*WF (Range)*
05/28	0.05	0.5 ± 0.16	*−11.0 ± 5.9*	*11.5 ± 5.9*	*2.6 - 5E-05 (0.7) (1.5E-05)*	*0.28 (0.9−0.08)*
06/01	0.09	−4.0 ± 1.1	*−4.0 ± 5.9*	*0.1 ± 6.0*	*3.1 - 5E-05 (0.9) (1.5E-05)*	*0.17 (0.5−0.05)*
06/30	0.09	3.3 ± 0.9	*−15.9 ± 5.9*	*19.2 ± 6.0*	*3.0 - 5E-05 (0.9) (1.5E-05)*	*0.53 (1.6−0.14)*
07/21	0.16	−0.3 ± 0.4	*−9.1 ± 5.9*	*8.7 ± 5.9*	*4.0 - 5E-05 (1.2) (1.5E-05)*	*0.69 (2.1−0.19)*
08/23	0.20	0.1 ± 0.66	*−4.2 ± 5.9*	*4.3 ± 5.9*	*4.6 - 5E-05 (1.3) (1.5E-05)*	*0.44 (1.3−0.12)*

All numbers reported in $\mu g\ m^{-2}\ d^{-1}$. Italicized data are calculated values. SD = standard deviation.

density, temperature, moisture and biological activity will be different than that encountered in the field. There have been successful attempts to estimate field mechanisms of NO production and consumption from laboratory measurements [*Galbally and Johansson*, 1989; *van Dijk et al.*, 2002]. Furthermore, we applied our laboratory derived model to field measurement and see a reasonable estimate of field consumption (Figure 3). Finally, our consumption estimates for the 1999 field season (2.6 and 19.2 $\mu g\ CH_3Br\ m^{-2}\ d^{-1}$) encompass the rate reported by *Serça et al.* [1995] for a temperate forest soil in Colorado.

[16] Soil production estimates calculated from the difference between net field measurements and the modeled consumption in the forest soil range from 0.05 to 19.2 $\mu g\ CH_3Br\ m^{-2}\ d^{-1}$. These overlap with the range of net positive flux measurements reported by *Rhew et al.* [2001] for Southern California shrubland (0.03−14.7 $\mu g\ m^{-2}\ d^{-1}$) and *Dimmer et al.* [2001] for a conifer forested peatland in Ireland (0.08 to 18 $\mu g\ m^{-2}\ d^{-1}$).

4.3. Sources of CH_3Br

[17] Production of CH_3Br in a temperate forest soil could be the result of abiotic [*Keppler et al.*, 2000], fungal [*Harper*, 1985; L-TH2000, KR2003] or other unidentified processes. *Keppler et al.* [2001] present an abiotic mechanism for production of halocarbons during the oxidation of Fe^{3+} in the presence of organic matter. We do not have the information available to determine if this process occurs at our site.

[18] Fungi could also be responsible for the emission of CH_3Br from this soil. There was visual evidence throughout the sampling period of fungal mycelium, fruiting bodies and ectomycorrhizal. We predicted production of CH_3Br by ectomycorrhizal fungi (EF) in the College Woods soils based on observations by KR2003. Their observations for *Cenococcum geophilium* revealed a linear increase in CH_3Br production rates with halide content in the media. We calculated a simple linear increase in production between 0.02 mM and 20 mM Br^- in media for both the highest (*Laccaria laccata*) and lowest (*Hebeloma crustuliniforme*) observed production rates and determined the rates in our soil based on the Br^- content of the surface soil on 5 sampling days. Fungal production by EF ($\mu g\ CH_3Br\ m^{-2}\ d^{-1}$) was estimated using the following equation:

$$EF_{CH_3Br} = \frac{\left[\frac{ugCH_3Br}{g_{fungi}d} * g_{fungi}\right]}{A_c} \quad (2)$$

The mass of fungi (g_{fungi}) in the collar was estimated as the fungal biomass in $g_{fungi}\ kg_{dry\ soil}^{-1}$ multiplied by the grams of dry soil in the collar. Fungal biomass 50.7 ± 18.4 $\mu g_{fungi}\ g_{org.\ matter}^{-1}$ was an average of the fungal biomass measured in a northern hardwood forest stand of similar age and species composition [*Taylor et al.*, 1999]. Conservatively, we believe half of the total fungal biomass to be EF. Fungal biomass was then calculated as 0.34 ± 0.25 g fungi in the collar area. Organic matter content in the collar was measured as 60.3%. A_c, collar area, is 0.397 m^2.

[19] The CH_3Br produced by wood-rotting fungi was estimated using equation (3) modified from L-TH2000:

$$WF_{CH_3Br} = D^*[Br^-]^*10^{12} * k_{fc}^*\left(\frac{m_{CH_3Br}}{m_{Br^-}}\right) \quad (3)$$

D is the annual pre-agricultural decomposition rate ($kg_{dry\ matter}\ m^{-2}\ yr^{-1}$). Assuming steady state with decomposition equal to production, this value (0.448 $kg\ m^{-2}\ yr^{-1}$) was based on the annual litter production rates calculated from direct measurements by *Matthews* [1997] for cool-deciduous forests with evergreens. $[Br^-]$ is the measured bromide concentration in the high organic matter soil below the litter surface and falls within the range reported by L-TH2000 for litter. The net efficiency of fungal conversion of Br^- to CH_3Br, k_{fc}, was calculated as 0.021 according to parameters for temperate regions given in L-TH2000. m_{CH3Br} and m_{Br^-} are the molar mass of CH_3Br and Br^-.

[20] Estimates from EF and WF indicate that they could be responsible for some of the production of CH_3Br in these soils (Table 1). The error of the Gaussian fit controls the soil production error and is high due to the limited number of temperature and moisture manipulations. The Gaussian fit, a smoothed peak, may overestimate uptake rates when soil moisture is between 75 and 150% and when temperatures are between 10 and 25°C (Figures 2A and 2B). This may account for some of the differences between measured and modeled uptake (Figure 3).

[21] The range of EF production of CH_3Br in Table 1 is driven by our fungal mass estimate, the Br^- content of the soil and the high and low estimates reported by KR2003. EF may subsist on leaf or litter tissue which may have a higher Br^- content [e.g. L-TH2000 and references therein]. We assumed that half of the total fungal biomass in the collar is EF. Total fungal biomass can vary seasonally due to varying substrate availability, soil temperature and soil moisture of the system [*Myers et al.*, 2001]. Fungal biomass can also vary spatially on a local scale based on topography and disturbances such as tree fall [*Morris and Boerner*, 1999].

[22] Our calculations for the WF production of CH_3Br are +3 and −0.27 times the production estimate. L-TH2000 believe this is a conservative estimate because 25 to 40% of the global woody decay is not included and their estimates

use production by one species of fungi and therefore a single ratio of Cl/Br emission. KR2003 have measured differing ratios of halide ion production from one species to the next. We feel that our estimate is conservative and could result in a larger range of emission if the above issues were addressed.

4.4. Global Extrapolation

[23] The net consumption rate of 168 ± 72 μg m^{-2} for the 1999 growing season extrapolated over a global area of 12.9×10^{12} m^2 for temperate forests [*Matthews*, 1983] yields an estimate of net uptake of 2.2 ± 0.9 Gg of CH_3Br yr^{-1}. This estimate is an order of magnitude less than the *Shorter et al.* [1995] and the *Serça et al.* [1998] estimates for temperate forest soil uptake of CH_3Br. Differences in measurement technique, sampling site characteristics or a production mechanism in the soil could all be responsible for the discrepancy between these estimates. Consumption rates change with temperature and moisture and therefore an estimate should take into account seasonal changes in consumption rate. The discrepancy between the estimates may reflect an abiotic or fungal production mechanism in the soil. The two estimates for fungal production from temperate forests: 0.5 to 5.2 Gg CH_3Br yr^{-1} from WF by L-TH2000 and 7 to 65 Gg yr^{-1} from EF by KR2003 could account for the difference between the estimates.

5. Conclusions

[24] Soils have a tremendous potential to consume CH_3Br and are currently identified as significant sinks in the tropospheric budget. Production of CH_3Br occurs in soils as well and can exceed consumption resulting in a net efflux of CH_3Br to the atmosphere. An abiotic mechanism during organic matter degradation and/or fungi associated with litter and/or tree roots may be responsible for this production. Both the consumption and production processes are important to our understanding of the natural cycling of CH_3Br and the net CH_3Br exchange with these systems.

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P. M. Crill, C. H. Mosedale, R. K. Varner, and M. L. White, Complex Systems Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824, USA. (ruth.varner@unh.edu)