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Measuring terrestrial fluxes of methyl chloride and methyl bromide using a stable isotope tracer technique

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[1] Atmospheric methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), compounds involved in the destruction of stratospheric ozone, are simultaneously produced and consumed by the terrestrial biosphere. Here we present a stable isotope incubation technique using $^{13}CH_3Cl$ and $^{13}CH_3Br$ as tracers to simultaneously determine production and consumption fluxes in boreal forest soils from Alaska, USA. Measured uptake rates are consistent with previously reported boreal soil results for CH_3Br and show a CH_3Cl:CH_3Br molar consumption ratio of 40:1. Boreal forest soils appear to produce small amounts of these methyl halides as well, but at rates that are negligible in their global budgets. This isotope tracer technique can be applied to laboratory studies of plants and other soils and to field measurements where disturbances to the system can be minimized. *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); 0394 Atmospheric Composition and Structure: Instruments and techniques; 1610 Global Change: Atmosphere (0315, 0325). **Citation:** Rhew, R. C., M. Aydin, and E. S. Saltzman, Measuring terrestrial fluxes of methyl chloride and methyl bromide using a stable isotope tracer technique, *Geophys. Res. Lett.*, *30*(21), 2103, doi:10.1029/2003GL018160, 2003.

1. Introduction

[2] CH_3Cl and CH_3Br are the primary carriers of natural chlorine and bromine to the stratosphere [*Penkett et al.*, 1980; *Schauffler et al.*, 1998], where they catalyze the destruction of stratospheric ozone. CH_3Br is also a broad-spectrum agricultural and structural fumigant that is subject to international regulation due to its ozone depleting potential [*UNEP*, 1995]. Atmospheric residence times of CH_3Cl and CH_3Br based on estimates of tropospheric sinks are $\sim$1.3 years and $\sim$0.7 years, respectively [*Montzka and Fraser*, 2003], although current estimates of the methyl halide emissions do not balance their losses suggesting that new sources need to be identified and/or that the sink terms need to be reduced.

[3] CH_3Br and CH_3Cl are consumed by anaerobic and aerobic microbial processes in soils [*Goodwin et al.*, 2001; *Hines et al.*, 1998; *McAnulla et al.*, 2001; *Oremland et al.*, 1994]. Aerobic soils are believed to be a major sink of atmospheric CH_3Br, with a global uptake rate estimated at 47 ± 32 Gg yr^{-1} [*Shorter et al.*, 1995; *Varner et al.*, 1999b], or roughly 20% of the total global sink strength. Estimates of the global CH_3Cl soil sink are highly uncertain, owing to a much smaller set of in situ and laboratory measurements. Plant leaves, roots, and stems demonstrate first order uptake rates of CH_3Br when exposed to high concentrations [*Jeffers et al.*, 1998], but it is unknown if such processes occur at ambient levels.

[4] Methyl halide emissions have been observed in situ from numerous terrestrial ecosystems, including freshwater wetlands, peatlands, conifer forest soils, coastal salt marshes, shrublands, and tropical forests [*Dimmer et al.*, 2001; *Rhew et al.*, 2001; *Rhew et al.*, 2000; *Varner et al.*, 1999a; *Yokouchi et al.*, 2002]. Emissions also have been observed from wood-rot fungi [*Harper*, 1985] and several crops, including rice paddies and *Brassica* plants [*Gan et al.*, 1998; *Redeker et al.*, 2000]. In addition, abiotic production mechanisms involving the degradation of organic matter [*Keppler et al.*, 2000] and the methylation of chloride by plant pectin [*Hamilton et al.*, 2003] have been identified, although these have not yet been observed under natural conditions.

[5] We have applied a stable isotope tracer technique to simultaneously determine terrestrial production and consumption rates of CH_3Br and CH_3Cl. The method described here is analogous to studies using ^{13}C or ^{14}C labeled methane to study simultaneous production and consumption of methane in soils [*Andersen et al.*, 1998; *von Fischer and Hedin*, 2002]. In addition, stable isotope tracer incubation techniques have been applied to separate biological and chemical degradation rates of CH_3Br and CH_3Cl in oceanic waters [*King and Saltzman*, 1997; *Tokarczyk et al.*, 2001; *Tokarczyk and Saltzman*, 2001].

2. Theory and Calculations

[6] Methyl halide flux measurements typically rely on laboratory incubations or field-based flux chambers. If production and consumption processes occur simultaneously, headspace concentrations will reflect the net result of these two processes. If a stable isotope $^{13}CH_3X$ (X = Cl or Br) spike is added to the headspace, simultaneous measurements of $^{12}CH_3X$ and $^{13}CH_3X$ concentrations can be used to solve for gross production rates (P) and uptake rate constants (k). The following equations describe the time-dependent behavior of isotopic CH_3X in such an experiment:

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Table 1. Boreal Forest Soil Incubation Experiments

Experiment/site	analysis (mm/dd/yy)	Temp (°C)	dry mass (g)	H_2O (% wet wt)	bulk dens (g/cc)
1. Control	9/12/02	22	0.0	0	0
Site A: Fairbanks, AK (64°53′N, 147°52′ W)					
2. run #1	9/24/02	22	46.4	20	0.7
3. run #2	9/24/02	22			
4. steam sterilized	10/09/02	23			
Site B: Caswell, AK (61°60′N, 150°03′ W)					
5. run #1	10/15/02	23	46.0	24	0.7
6. run #2	10/15/02	22			
7. steam sterilized	10/21/02	22			
Site C: Seward, AK (60°09′N, 149°26′ W)					
8. run #1	10/31/02	23	49.1	39	0.6
9. run #2	10/31/02	22			0.5
10. steam sterilized	11/01/02	22			0.5
Bonanza Creek Experimental Forest, Fairbanks AK (64°45′ N, 148°20′W)					
11. flux chamber with leaf litter, small aspen, birch, spruce saplings	9/4/97	14	–	n.d.	n.d.
12. flux chamber with leaf litter, unidentified mosses, mushrooms	9/4/97	13	–	n.d.	n.d.

Dry mass, H_2O % (wet weight basis) and bulk density (g/cc) were determined by drying the soil sample overnight at 80°C. Flux chamber measurements were conducted with the same methods described in *Rhew et al.* [2001].

$$\frac{d[^{12}CH_3X]}{dt} = (F_{12}) \times P - (k_{12})[^{12}CH_3X] \quad (1)$$

$$\frac{d[^{13}CH_3X]}{dt} = (F_{13}) \times P - (k_{13} + k_L)[^{13}CH_3X] \quad (2)$$

where bracketed terms are concentrations (pmol/mol), F is the relative fraction of P for each isotope ($F_{12} + F_{13} = 1$), and k_{12} and k_{13} are the first order consumption rate constants (min^{-1}). SF_6 and F-113 tracers are also injected to determine k_L, a small loss rate correction to account for diffusion of the added compounds through the soil pore space [*Andersen et al.*, 1998]. The solutions for equations 1 and 2 are:

$$[^{12}CH_3X]_t = \frac{(F_{12} \times P)}{k_{12}} - \left(\frac{(F_{12} \times P)}{k_{12}} - [^{12}CH_3X]_0\right) \cdot \exp\{-k_{12}(t - t_0)\} \quad (3)$$

$$[^{13}CH_3X]_t = \frac{(F_{13} \times P)}{(k_{13} + k_L)} - \left(\frac{(F_{13} \times P)}{(k_{13} + k_L)} - [^{13}CH_3X]_0\right) \cdot \exp\{-(k_{13} + k_L)(t - t_0)\} \quad (4)$$

where $[^{12}CH_3X]_0$ and $[^{13}CH_3X]_0$ are concentrations at the time (t_0) of the first sampling after closure. The uptake rate constants, k_{12} and k_{13}, are related by experimentally derived stable carbon isotopic fractionation factors ($\alpha = k_{12}/k_{13}$). We simultaneously solve for P, k_{12}, $[^{12}CH_3X]_0$ and $[^{13}CH_3X]_0$ in the above equations using concentration data for each carbon isotope pair of methyl halides ($^{12}CH_3{}^{79}Br$ and $^{13}CH_3{}^{79}Br$, $^{12}CH_3{}^{81}Br$ and $^{13}CH_3{}^{81}Br$, $^{12}CH_3{}^{35}Cl$ and $^{13}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$ and $^{13}CH_3{}^{37}Cl$) and by conducting a multidimensional unconstrained nonlinear minimization (Nelder-Mead) of the total weighted error, E, between predicted and observed values:

$$E = \sum_{t=1}^{n} \frac{\left(Y_{pred}(t) - Y_{obs}(t)\right)^2}{relative\ SD} + \sum_{t=1}^{n} \frac{\left(Z_{pred}(t) - Z_{obs}(t)\right)^2}{relative\ SD} \quad (5)$$

where Y represents $[^{12}CH_3X]$, Z represents $[^{13}CH_3X]$, n represents the number of measurements and *relative SD* refers to the standard deviation of the measurement divided by the concentration. *relative SD* is used as a weighting function (see *von Fischer and Hedin*, 2002, for a similar method). Calculations are made using Matlab software (Mathworks, Inc.).

[7] This method has the advantage of being relatively insensitive to the variability of observed fractionation factors. In this study, we use α values of 1.046 ± 0.004 for CH_3Cl and 1.038 ± 0.034 CH_3Br, which encompass the range of values observed from the oxidation of methyl halides by methylotrophic bacteria [*Miller et al.*, 2001] as well as the CH_3Br uptake fractionation value observed in agricultural soils [*Bill et al.*, 2002a]. This range in α increases the overall uncertainty of calculated fluxes by an average of 0.3 and 1.0 nmol m^{-2} d^{-1} for CH_3Br and CH_3Cl, respectively. We use a F_{12} value of 0.9893 ± 0.0002, the $^{12}C/(^{12}C+^{13}C)$ ratio equivalent to a $\delta^{13}C$ value of −40 ± 20‰ on the PDB scale [*Craig*, 1957], which is approximately the background atmospheric $\delta^{13}C$ value for CH_3Cl [*Thompson et al.*, 2002] and encompasses most of the known $\delta^{13}C$ values of CH_3Br and CH_3Cl sources [*Bill et al.*, 2002b; *Thompson et al.*, 2002].

[8] In order to calculate uptake rates for the boreal forest soil samples analyzed in this study, k is multiplied by background northern hemispheric atmospheric values of 11 ppt CH_3Br and 550 ppt CH_3Cl. Fluxes (nmol m^{-2} d^{-1}) are calculated using both a surface area method whereby production and consumption rates are divided by the exposed surface area of the soil in the incubation study, as well as a bulk density method (depth of uptake = 1 cm, bulk density of soils = 1.4 g cm^{-3}) to correspond with previous soil consumption studies [*Shorter et al.*, 1995; *Varner et al.*, 1999b].

3. Methods

[9] Surface soils (0–8 cm) were collected from 3 boreal forests in Alaska between 29 July and 3 August 2002 (Table 1), sealed in double polyethylene bags, and stored at 5°C until analysis. Sub-samples of the soil were packed

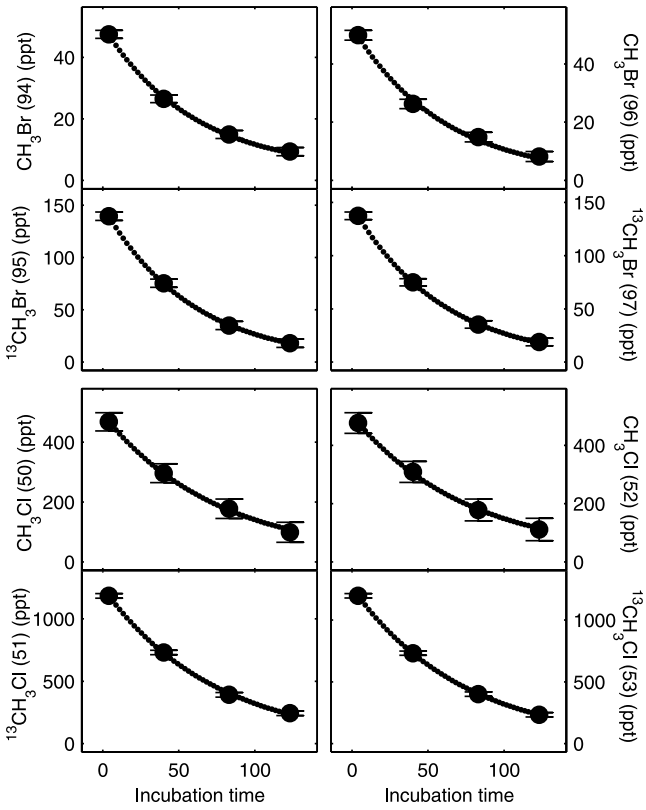

Figure 1. Concentrations of the stable isotopologues of CH_3Br (top panels) and CH_3Cl (bottom panels) versus time of enclosure (in minutes). These results are from a typical soil incubation (expt #6), following the addition of $^{13}CH_3Br$ and $^{13}CH_3Cl$. Curve fits include simultaneous production and consumption terms, their associated isotope fractionation effects, and the redistribution of the tracer in the chamber headspace. Error bars indicate uncertainties due to the system calibration.

lightly into a small glass container and placed inside a larger 1.9L glass jar at 22°C. After allowing the soils to equilibrate to ambient temperature and concentrations, the jar was sealed using a stainless steel lid with a viton gasket. A known amount of $^{13}CH_3Br$, $^{13}CH_3Cl$, SF_6 and F-113 was injected through a septum in the lid to bring initial concentrations to roughly 100 ppt, 1000 ppt, 800 ppt, and 1200 ppt, respectively. Headspace samples were drawn from the incubation chamber into a previously evacuated stainless steel loop (~25 cc) at intervals of 40 minutes over 2 hours. Soil samples were measured twice consecutively, then steam sterilized by heating the covered soils to 85–90° C for one hour, and an incubation experiment was later conducted on the sterile soil.

[10] Gas samples were measured on a capillary gas chromatograph/mass spectrometer (Agilent 5890/5973) system optimized for low volume air samples [*Aydin et al.*, 2002]. Calibration standards for both ^{12}C and ^{13}C methyl halides (Isotec, Aldrich, and Scott Gases) were produced gravimetrically using a two-step dilution technique, with an overall accuracy estimated at 2% for CH_3Br and CH_3Cl. The four stable isotopologues of CH_3Br ($^{12}CH_3{}^{79}Br$, $^{12}CH_3{}^{81}Br$, $^{13}CH_3{}^{79}Br$, and $^{13}CH_3{}^{81}Br$) and four isotopologues of CH_3Cl ($^{12}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$, $^{13}CH_3{}^{35}Cl$, and $^{13}CH_3{}^{37}Cl$) were detected by selected ion monitoring of the parent ions (m/z = 94–97 and 50–53, respectively). Simultaneous measurement of all 4 isotopologues of CH_3X on the quadrupole mass spectrometer is complicated by the ion fragmentation pattern of each analyte. For example, $^{13}CH_2X^+$ yields the same mass to charge ratio as $^{12}CH_3X^+$. In ambient samples, the $^{12}CH_3X$ peak areas contributed by $^{13}CH_3Br$ (for m/z = 94 or 96) and $^{13}CH_3Cl$ (for m/z = 50 or 52) are typically negligible. However, in these isotope tracer studies, $^{13}CH_3X$ ion fragments contributed significantly to the $^{12}CH_3X$ peak areas. Corrections were applied by using experimentally determined $^{12}CH_3X$ and $^{13}CH_3X$ ion fragmentation ratios [*King*, 1997].

4. Results and Discussion

[11] CH_3Cl and CH_3Br were consumed by all boreal forest soil samples (Figure 1), with an average CH_3Cl:CH_3Br molar uptake ratio of 39 ± 4. The correlation between CH_3Cl and CH_3Br consumption rates reported here is similar to the ratio of uptake rates measured in southern California shrublands (~40:1) [*Rhew et al.*, 2001]. If this 40:1 molar ratio applies to all biomes and soils consume 47 Gg yr^{-1} of CH_3Br globally, then soils are predicted to consume 1.0 Tg CH_3Cl yr^{-1}, five times the currently

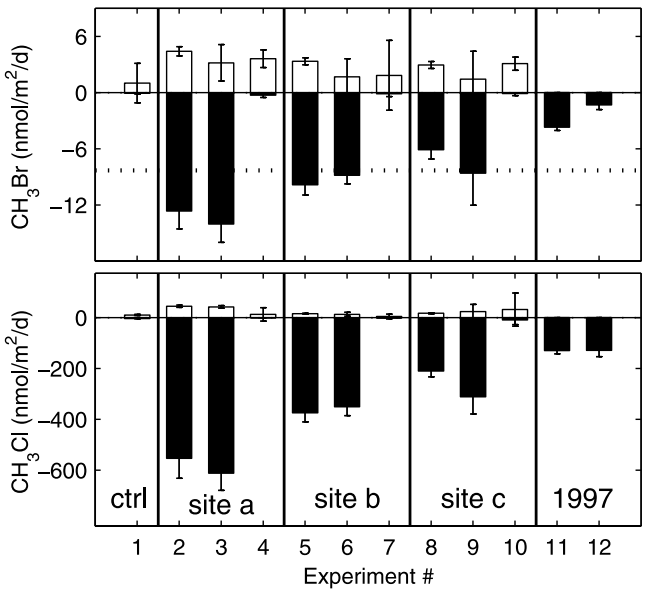

Figure 2. Simultaneous production (white bars) and consumption (black bars) of CH_3Br and CH_3Cl determined using the stable isotope tracer technique. Each bar represents the average calculated flux using both stable isotopologues of the parent ions (m/z = 94 & 96 for CH_3Br, 50 & 52 for CH_3Cl), with error bars representing the range of values plus their associated experimental errors. Consecutive experimental runs of the same soil sample yield consistent results, except for site C soils which were analyzed at different bulk densities. The third run for each site followed steam sterilization. The 1997 bars represent surface net fluxes from an Alaskan boreal forest. The dashed line represents *Shorter et al.* [1995] results for CH_3Br.

estimated CH_3Cl soil sink [*Khalil and Rasmussen*, 2000; *Montzka and Fraser*, 2003].

[12] Average CH_3Br consumption rates in the boreal forest soils (surface area method) were 9.9 ± 2.8 nmol m^{-2} d^{-1} (Figure 2), consistent with the 8.3 ± 0.2 nmol m^{-2} d^{-1} value reported for boreal soils from Manitoba, Canada [*Shorter et al.*, 1995]. CH_3Cl uptake rates were 400 ± 150 nmol m^{-2} d^{-1}. In contrast, uptake rates in steam sterilized soils were <2% of unsterilized soils, indicating that consumption processes are predominantly biological [*Hines et al.*, 1998; *Shorter et al.*, 1995] rather than chemical. Fluxes calculated with the bulk density method yielded values that were 73 ± 2% of those calculated with the surface area method. In each experiment, the calculated uptake fluxes for the halogen isotope pairs ($^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$, for example) agreed to within 0.5 nmol m^{-2} d^{-1} for CH_3Br and 25 nmol m^{-2} d^{-1} for CH_3Cl, without a noticeable bias for lighter or heavier halogen isotopologue. Consecutive analyses of the same soil under the same conditions (sites A and B) agreed to within 10%. However, the soil from site C was more loosely packed in the second analysis and showed 30–40% higher uptake rates for CH_3Br and CH_3Cl, suggesting that fluxes are sensitive to the degree of soil packing.

[13] These uptake rates are significantly larger than the net fluxes measured in two 1997 flux chamber experiments in an Alaska boreal forest (last two bars in Figure 2). There are several possibilities for the discrepancy: different sampling sites have different uptake rates; lower field temperatures lead to lower biologically mediated uptake rates; simultaneous production by the enclosed plant, soil, or fungal material leads to lower net consumption rates; and/or the laboratory conditions utilize disturbed soil samples that may have higher exposed surface area than expected under natural conditions, thus providing more active sites for degradation [*Harper et al.*, 2000].

[14] Our measurements suggest that production of methyl halides occurred in the boreal forest soils at average rates of 2.5 ± 1.4 nmol CH_3Br m^{-2} d^{-1} and 24 ± 14 nmol CH_3Cl m^{-2} d^{-1}, although the control experiment with no soil yielded roughly half this production rate. Steam sterilized soils showed slightly larger production rates of 3.2 ± 0.5 nmol CH_3Br m^{-2} d^{-1} and 31 ± 32 nmol CH_3Cl m^{-2} d^{-1}. These observed emissions may be evidence for the abiotic formation of methyl halides in soils [*Keppler et al.*, 2000], but it is not known if the process of heating soils artificially created precursors that subsequently evolved into methyl halides. A crude extrapolation for potential methyl halide production in boreal forest soils (12.0×10^{12} m^2 for 180 active days per year) yields 0.5 ± 0.3 Gg CH_3Br yr^{-1} and 2.6 ± 1.5 Gg CH_3Cl yr^{-1}, which are negligible quantities in their global budgets.

[15] The isotope tracer technique provides an unambiguous determination of soil uptake rates at near-ambient concentrations. This stable isotope tracer method can be applied to laboratory incubations to investigate the CH_3Cl:CH_3Br uptake ratios in soils, uptake of CH_3X by plants, and microbial transhalogenation in anoxic soils. In addition, this stable isotope tracer method can be applied to in situ flux chamber measurements that include vegetation or fungi along with soils, thus providing a method to separate production and consumption processes in the field rather than physically separating a system into its individual components, a process that may significantly alter the dynamics of the system.

[16] **Acknowledgments.** We thank W. Reeburgh for assistance with flux chamber measurements and F. Primeau for computing advice. Research was supported by NSF and the NOAA Postdoctoral Program in Climate and Global Change, administered by the University Corporation for Atmospheric Research.

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