

## Stable carbon isotope composition of atmospheric methyl bromide

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[1] Methyl bromide ( $\text{CH}_3\text{Br}$ ) constitutes the largest source of bromine atoms to the stratosphere and plays an important role in stratospheric ozone depletion. However, the  $\text{CH}_3\text{Br}$  atmospheric budget remains uncertain. We report the first measurements of stable carbon isotope ratios for atmospheric  $\text{CH}_3\text{Br}$  and explore the constraints they provide for the atmospheric budget. The measured  $\delta^{13}\text{C}$  of  $\text{CH}_3\text{Br}$  ranged from  $-44.8\text{‰}$  to  $-41.2\text{‰}$  (mean value  $-43.1\text{‰}$ ,  $N = 7$ ). This isotopic value is less negative than the anthropogenic source signature ( $-53.2$  to  $-47.5\text{‰}$ ), but is indistinguishable from the only quantified natural source signature ( $-43.0\text{‰}$ ). Based on known source signatures and our atmospheric measurements, we predict that the mean kinetic isotope effect associated with sinks must be small (2–4‰). We further estimate that a total phaseout of anthropogenic sources would likely change the isotopic composition of atmospheric  $\text{CH}_3\text{Br}$  by 2–4‰, and that this change would be difficult to detect with current measurement techniques.

**INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1040 Geochemistry: Isotopic composition/chemistry; 1615 Global Change: Biogeochemical processes (4805). **Citation:** Bill, M., M. E. Conrad, and A. H. Goldstein (2004), Stable carbon isotope composition of atmospheric methyl bromide, *Geophys. Res. Lett.*, 31, L04109, doi:10.1029/2003GL018639.

### 1. Introduction

[2] Bromine radicals contribute significantly to stratospheric ozone loss through coupled reactions with  $\text{ClO}$ ,  $\text{HO}_2$ , and  $\text{NO}_2$  radicals [e.g., *Wofsy et al.*, 1975; *McElroy et al.*, 1986]. The largest source of bromine to the stratosphere is methyl bromide ( $\text{CH}_3\text{Br}$ ).  $\text{CH}_3\text{Br}$  has a tropospheric concentration of about 10 pptv, the highest concentration of any long lived organobromide [*Kurylo et al.*, 1999], and a total lifetime in the atmosphere of 0.6 to 0.9 years. Unlike chlorofluorocarbons,  $\text{CH}_3\text{Br}$  is produced by both anthropogenic and natural processes. Our knowl-

edge of the  $\text{CH}_3\text{Br}$  atmospheric budget remains unbalanced as the magnitude of various sources and sinks are still uncertain [e.g., *Kurylo et al.*, 1999]. An isotope mass balance approach has been proposed to constrain the  $\text{CH}_3\text{Br}$  atmospheric budget by analyzing the source signatures and the isotopic fractionations associated with sinks [*McCauley et al.*, 1999]. The isotopic composition of atmospheric  $\text{CH}_3\text{Br}$  will reflect the weighted average isotopic signature of all the sources, and the weighted average kinetic isotope effect of all the loss mechanisms, contributing to the measured sample:

$$\delta^{13}\text{C}^{\text{atm}} = \sum_{i=1}^n \Phi_i^{\text{source}} \delta^{13}\text{C}_i^{\text{source}} + \sum_{j=1}^n \Phi_j^{\text{sink}} \varepsilon_j^{\text{sink}} \quad (1)$$

where  $\delta^{13}\text{C}^{\text{atm}}$  and  $\delta^{13}\text{C}^{\text{sources}}$  are respectively, the carbon isotope compositions of  $\text{CH}_3\text{Br}$  in the atmosphere and of the different sources in per mil.  $\Phi$  is the  $\text{CH}_3\text{Br}$  flux fraction for each source and sink.  $\varepsilon$  is the kinetic isotope effect (KIE) of the different sinks expressed in per mil as:

$$\varepsilon = 1000(r_c - 1) \quad (2)$$

$r_c$  is defined as the ratio of the rate constant for the reaction removing  $^{12}\text{CH}_3\text{Br}$  to that for removal reaction with  $^{13}\text{CH}_3\text{Br}$ .

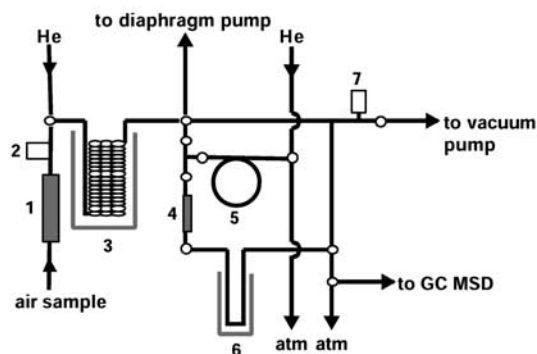
[3] Up to now, the carbon isotope composition of atmospheric  $\text{CH}_3\text{Br}$  had not been measured due to its low atmospheric mixing ratio (10 pptv) and the relatively high amount of carbon needed for the isotopic analysis. Measurement of carbon isotope ratios in organic trace gases using our current technology with the Micromass Isoprime gas chromatograph isotope ratio mass spectrometer (GC-IRMS) requires 5 nanograms of carbon, roughly corresponding to 1000 liters of air having a mixing ratio of  $\sim 10$  pptv of  $\text{CH}_3\text{Br}$ . Here we report the first measurements of stable carbon isotope ratios of atmospheric  $\text{CH}_3\text{Br}$  and explore how they could be used to constrain knowledge of the atmospheric budget.

### 2. Experiment

#### 2.1. Sampling

[4] Carbon isotopic composition of atmospheric  $\text{CH}_3\text{Br}$  was measured in an urban area close to the coast of the Pacific ocean at Berkeley ( $37^\circ 52.39'\text{N}$ ,  $122^\circ 15.85'\text{W}$ , 113 meters elevation), California, on 6 days from September 27 to October 31 2002. Ambient air temperatures ranged

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**Figure 1.** Instrumental configuration of high flow sampling line: 1. Drierite trap; 2. Flow controller; 3. Glass coil trap used for initial preconcentration; 4. Magnesium perchlorate trap; 5.  $\frac{1}{4}$  inch Tenax TA packed glass column; 6.  $\frac{1}{4}$  inch glass tube trap placed in liquid Argon for cryofocusing sample; 7. Vacuum gauge.

from 13.5°C at dawn to 25.5°C during the sampling time. We developed and tested a high flow sampling line for trapping atmospheric  $\text{CH}_3\text{Br}$  (Figure 1). Air was sampled at 6.9 L/min for  $\sim 3$  hours using a vacuum pump pulling through a glass trap ( $\sim 8$  meters length  $\times$   $\frac{1}{4}$ -inch diameter) placed in liquid argon at  $-186^\circ\text{C}$ . The concentrated sample was then transferred to a  $\frac{1}{4}$ -inch Tenax TA packed column (0.4 meters length  $\times$   $\frac{1}{4}$ -inch diameter) by warming at room temperature and flushing the glass trap with ultra-pure helium.  $\text{CH}_3\text{Br}$  was adsorbed in the Tenax TA column at room temperature whereas the  $\text{CO}_2$  went through the Tenax TA column. By backflushing with ultra-pure helium and heating the column at  $\sim 128^\circ\text{C}$ , the sample was transferred to a glass tube placed in liquid argon ( $-186^\circ\text{C}$ ). Water was removed using a magnesium perchlorate trap during the sample transfer. The non condensable gases were pumped away and the two ends of the U-glass tube were sealed using a torch then the sample was stored in liquid nitrogen for later analysis.

[5] The trapping efficiency for this system was tested by creating ambient level standards (diluting  $\text{CH}_3\text{Br}$  from a 2.8 ppbv standard into pure air produced using an AADCO zero air generator) then pre-concentrating them at a flow of 7 L/min. Tests with ambient level standard dilutions yielded  $97 \pm 8\%$  ( $1\sigma$ ;  $n = 6$ ) recovery for sample volumes ranging from 196 L to 938 L.

## 2.2. Carbon Isotope Measurements

[6] The pre-concentrated samples in the glass tubes were introduced into the gas chromatograph isotope ratio mass spectrometer (GC-IRMS) by cracking them in bellow crackers and flushing the sample tube with ultra-pure helium (Figure 2). The pre-concentrated sample was transferred to a 0.4 mm diameter 370  $\mu\text{L}$  volume Silcosteel loop placed in liquid nitrogen and mounted on a 6-port valve (Valco). Samples were injected into the gas chromatograph by switching the 6-port valve and heating the loop with hot water ( $\sim 50^\circ\text{C}$ ). Gases were separated chromatographically on a GasPro fused silica capillary column (60 m  $\times$  0.32 mm). After GC separation, the  $\text{CH}_3\text{Br}$  was combusted to  $\text{CO}_2$ , water was removed, and the carbon isotope ratio

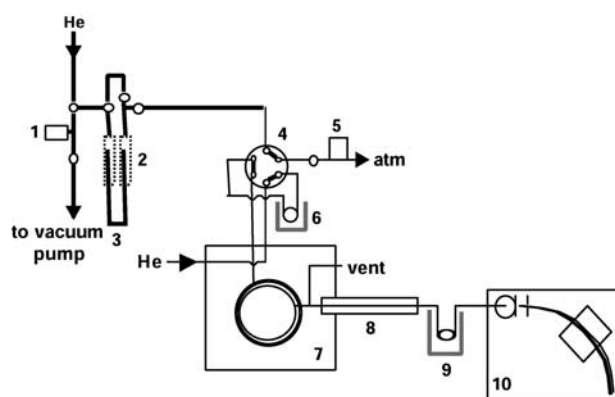
was measured in the mass spectrometer. Other gases were transferred by a heart split to a vent to keep the background in the IRMS low. Stable carbon isotope ratios are expressed in the conventional  $\delta$ -notation in parts per mil (‰) relative to the Peedee Belemnite (PDB) standard:

$$\delta^{13}\text{C} = \left[ \left( \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \right) \right] \times 1000 \quad (3)$$

Analytical precision was estimated by sampling different quantities of air standards with ambient levels of  $\text{CH}_3\text{Br}$  at a flow of 7 L/min. Repeated trapping experiment of ambient level dilutions from a  $\text{CH}_3\text{Br}$  standard (Scott 2.8 ppbv) yielded values of  $50.9 \pm 2.2\%$  ( $1\sigma$ ;  $n = 6$ ) for concentrations ranging from 11.8 to 60 pptv and corresponding to 6 and 14 ng of  $\text{CH}_3\text{Br}$  carbon. Dilutions of another  $\text{CH}_3\text{Br}$  standard with lower  $\delta^{13}\text{C}$  (Scott 1ppmv) yielded a value of  $-57.0 \pm 1.2\%$  ( $1\sigma$ ;  $n = 6$ ) for standard sizes ranging from 4.9 to 14.6 ng of  $\text{CH}_3\text{Br}$  carbon. Absolute calibration of the  $\delta^{13}\text{C}$  in  $\text{CO}_2$  produced from the combustion of  $\text{CH}_3\text{Br}$  was done by analyzing  $\text{CO}_2$  reference gas on the IRMS before each  $\text{CH}_3\text{Br}$  sample was analyzed. The  $\text{CO}_2$  reference gas was calibrated against National Institute of Standards and Technology (NIST)  $\text{CO}_2$  standards RM 8562  $\delta^{13}\text{C} = -3.76\%$ , RM 8563  $\delta^{13}\text{C} = -41.56\%$  and RM 8564  $\delta^{13}\text{C} = -10.45\%$ . Absolute accuracy of our measurements was limited by the analytical errors associated with the sampling line rather than by the accuracy of our method of standardization.

## 2.3. Concentration

[7]  $\text{CH}_3\text{Br}$  concentrations were determined using the mass 44 ( $\text{CO}_2$ ) area peak of the combusted  $\text{CH}_3\text{Br}$  as measured by the GC-C-IRMS. The response factor was determined by injecting known quantities of  $\text{CH}_3\text{Br}$  into the GC-C-IRMS. The analytical uncertainty for  $\text{CH}_3\text{Br}$  concentrations was mainly determined by the high flow sampling line and the precision of the response factor. Analytical



**Figure 2.** Instrumental configuration of sample introduction and analysis on the GC-C-IRMS system: 1. Vacuum gauge; 2. Bellow crackers; 3. Sample in a  $\frac{1}{4}$  inch glass tube; 4. 6-port valve for loading trap and then injecting samples; 5. Flow controller; 6. Silcosteel trap for cryofocusing sample; 7. Gas chromatograph; 8. Combustion reactor; 9. Water trap; 10. Isotope ratio mass spectrometer.

**Table 1.** CH<sub>3</sub>Br Mixing Ratio and  $\delta^{13}\text{C}$  Value Measured at Berkeley From End of September to October 2002

Date (day.month.year)	Concentration $\pm 1\sigma$ (ppt)	$\delta^{13}\text{C}_{\text{PDB}}$ of CH <sub>3</sub> Br $\pm 1\sigma$ (per mil)
27.09.2002	16.1 $\pm$ 2.4	-42.2 $\pm$ 2.0
11.10.2002	18.2 $\pm$ 2.7	-41.2 $\pm$ 2.0
14.10.2002	13.5 $\pm$ 2.0	-43.9 $\pm$ 2.0
16.10.2002	14.7 $\pm$ 2.2	-44.1 $\pm$ 2.0
22.10.2002	14.0 $\pm$ 2.1	-44.8 $\pm$ 2.0
23.10.2002	12.9 $\pm$ 1.9	-44.2 $\pm$ 2.0
31.10.2002	10.1 $\pm$ 1.5	-41.4 $\pm$ 2.0
Mean	14.2	-43.1
St deviation ( $1\sigma$ )	2.5	1.5

uncertainty from repeated trapping experiments with known quantities of CH<sub>3</sub>Br was  $\pm -15\%$ .

### 3. Results and Discussion

[8] Seven measurements of atmospheric CH<sub>3</sub>Br were made in Fall 2002, with an average of observed  $\delta^{13}\text{C}$  of  $-43.1\text{‰} \pm 1.5$  ( $1\sigma$ ) and a range from  $-44.8\text{‰}$  to  $-41.2\text{‰}$  (Table 1). The observed variation in the atmosphere was smaller than the analytical error we estimated for the technique. The average atmospheric mixing ratio was  $14.2 \text{ ppt} \pm 2.5$ , with a range from 18.2 to 10.1 ppt (Table 1). This average is higher than the atmospheric mixing ratio of the coastal northeastern Pacific Ocean measured by *Lobert et al.* [1995] (10 to 12 ppt) and *King et al.* [2000] ( $12.16 \text{ ppt} \pm 0.16$ ). Higher concentrations may be due to local sources such as salt marshes, field fumigation and/or production in coastal Pacific Ocean water. This data set is quite limited and more measurements are needed to determine if the data reflect hemispheric and global values. However, these are the first measurements of  $\delta^{13}\text{C}$  for ambient CH<sub>3</sub>Br, and it is instructive to determine what these initial results can tell us about the atmospheric isotope mass balance for CH<sub>3</sub>Br.

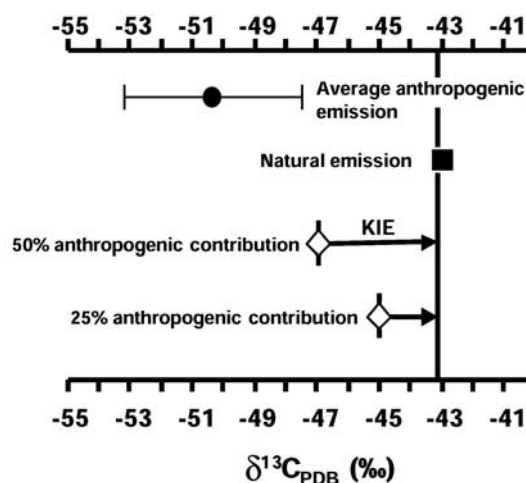
[9] The isotopic signature of several sources and sinks of CH<sub>3</sub>Br have been measured. The  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br that we measured ( $-43.1\text{‰} \pm 1.5$ ) is indistinguishable from the daily mean  $\delta^{13}\text{C}$  of CH<sub>3</sub>Br emitted from salt marsh plants ( $-43\text{‰} \pm 2$ ) [*Bill et al.*, 2002b]. The isotopic composition of emissions from the ocean (major source), non-salt marsh plants (source strength highly uncertain), and biomass burning (major source) have yet to be measured. The  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br is also in the range of the  $\delta^{13}\text{C}$  of CH<sub>3</sub>Br emitted from field fumigation which varied from  $-52.8$  to  $-42\text{‰}$  depending on the fraction of applied CH<sub>3</sub>Br that escaped to the atmosphere [*Bill et al.*, 2002a]. However the  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br is higher than the weighted mean  $\delta^{13}\text{C}$   $-54.4\text{‰}$  (ranging from  $-62.3\text{‰}$  to  $-52.9$ ) of the industrially produced CH<sub>3</sub>Br from the three largest manufacturers worldwide [*McCauley et al.*, 1999]. The weighted mean for all anthropogenic CH<sub>3</sub>Br emitted from direct emissions (fumigation of harvested crops and structures) and field fumigation ranges from  $-53.2$  to  $-47.5\text{‰}$  [*Bill et al.*, 2002a], and for the purpose of discussion in this manuscript, we estimate the mean value to be in the middle of that range,  $-50.4\text{‰}$  (Figure 3). Also for the purpose of discussion, we assume that the daily mean isotopic composition of salt marsh

emissions is representative of all natural sources even though there are not sufficient data available to test this assumption (Figure 3).

[10] The KIE of the photochemical loss processes in the atmosphere (oxidation by OH in the troposphere is the dominant loss process), and uptake by the ocean have also not been measured. The apparent KIE of soil uptake for CH<sub>3</sub>Br in fumigated fields has been measured at  $12\text{‰}$  [*Bill et al.*, 2002a], although this may not represent the KIE which occurs during soil consumption at background atmospheric concentrations. The KIE associated with consumption by three strains of methylotrophic bacteria have also been measured, and ranged from 4 to  $72\text{‰}$  [*Miller et al.*, 2001].

[11] These natural and anthropogenic signatures are used in Figure 3 to illustrate the isotope mass balance (equation 1) between the  $\delta^{13}\text{C}$  of CH<sub>3</sub>Br sources, the  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br and to derive a global KIE associated with the loss processes. We estimate that the weighted mean  $\delta^{13}\text{C}$  of all known sources is approximately  $-47\text{‰}$  assuming the anthropogenic sources contribute 50% of the total emissions. If anthropogenic sources only contribute 25% to the total emissions, then the weighted mean  $\delta^{13}\text{C}$  of all known sources would be closer to  $-45\text{‰}$ . To close the isotope mass balance, the KIE associated with sinks on average must therefore be of order 2–4‰ (Figure 3). A larger KIE would require a lighter source of CH<sub>3</sub>Br than has been measured thus far. If our assumptions and estimations are correct, reducing industrial emissions will increase  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br by approximately  $0.07\text{‰}$  per 1% reduction in industrial source fraction of the total budget, and completely eliminating industrially emitted CH<sub>3</sub>Br should increase the  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br by of order 2–4‰.

[12] *Yokouchi et al.* [2002] measured an annual decrease of 4 to 6% in CH<sub>3</sub>Br mixing ratio at a ground station in the Arctic (from mid-1996 to early 2002) and in the free troposphere at mid-latitude (from early 1999 to early 2002). *Montzka et al.* [2003] also reported a decrease in



**Figure 3.** Average  $\delta^{13}\text{C}$  of known sources and the inferred KIE associated with sinks after *Bill et al.* [2002a], *Bill et al.* [2002b] and *McCauley et al.* [1999]. Vertical line indicates the  $\delta^{13}\text{C}$  of atmospheric CH<sub>3</sub>Br and arrows indicate the KIE required for closing the isotope mass balance.

the global annual mean CH<sub>3</sub>Br mixing ratio between 1995–1997 and 2002 of about 13%. If the observed mixing ratio decrease was associated solely with a reduction in anthropogenic emissions, and the emissions in 1996 were 40–45% anthropogenic [Montzka *et al.*, 2003], these observations suggest a change in the percentage anthropogenic contribution to total emissions of approximately 8 to 26%, and this decrease in mixing ratios should have corresponded to an increase of approximately 0.6 to 1.8‰ in δ<sup>13</sup>C of atmospheric CH<sub>3</sub>Br.

#### 4. Conclusions

[13] We developed a method to analyze carbon isotopes of CH<sub>3</sub>Br in ambient air, and made the first measurements of carbon isotope composition of atmospheric organic components at a concentration of approximately 10 pptv. We determined the δ<sup>13</sup>C<sub>PDB</sub> value of atmospheric CH<sub>3</sub>Br to be −43.0‰ ± 1.5 (n = 7). This data set is still very limited. More measurements are needed to determine if these initial local data reflect hemispheric and global values.

[14] In order to reliably utilize the stable carbon isotope approach for constraining the global budget, the next steps would include quantifying the signatures of biomass burning emissions and oceanic emissions, measuring the kinetic isotope effect associated with oxidation by hydroxyl radicals in the atmosphere, and monitoring the isotopic composition of atmospheric CH<sub>3</sub>Br over a larger temporal and spatial scale. However, assuming our estimate of the anthropogenic and natural source signatures are correct, our atmospheric δ<sup>13</sup>C CH<sub>3</sub>Br measurement is representative, and the anthropogenic sources are now 25 to 50% of the total source, the expected change in δ<sup>13</sup>C of atmospheric CH<sub>3</sub>Br due to a total phaseout of anthropogenic sources would be of order 2–4‰, and our current measurement uncertainty of 1–2‰ would make this change difficult to detect. Our current knowledge of the C isotope budget for atmospheric CH<sub>3</sub>Br suggests that the KIE of all loss processes is in the range 2–4‰. If the KIE for loss processes were actually zero, it would infer that the average natural source signature could be 2–4‰ heavier than we assumed based on the salt marsh emission measurements, and that the atmospheric change in isotopic composition associated with a total phaseout of anthropogenic sources would be 4–8‰. If the average natural source signature were lighter than salt marsh emissions, this would imply a larger KIE for the loss processes and suggest that a total

anthropogenic phaseout would cause an even smaller and less detectible change in δ<sup>13</sup>C of atmospheric CH<sub>3</sub>Br.

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