Carbon isotope ratios of methyl bromide and methyl chloride emitted from a coastal salt marsh

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[1]   Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) play important roles in stratospheric ozone depletion, but their atmospheric budgets have large uncertainties. The analysis of stable isotope composition of methyl halides may provide useful independent information for further constraining their budgets. Here we report the first measurements of CH_3Br and CH_3Cl stable carbon isotope ratios emitted from a biogenic source under *in situ* conditions. CH_3Br and CH_3Cl emissions from the salt marsh plant *Batis maritima* showed a strong diurnal variation in $\delta^{13}C$, from $-65‰$ during the daytime to $-12‰$ at night. The minimum $\delta^{13}C$ values were observed at midday, coinciding with the time of greatest emissions and ambient temperature. At night, when the emissions were much smaller, the stable carbon isotopic ratios of CH_3Br and CH_3Cl became enriched in ^{13}C. The daily mean $\delta^{13}C$ of CH_3Br and CH_3Cl emissions, weighted by emission rate, were $-43‰$ and $-62‰$ respectively.   *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805)

1.   Introduction

[2]   Methyl bromide (CH_3Br) constitutes the largest source of bromine atoms to the stratosphere, and methyl chloride (CH_3Cl) is the most abundant halocarbon in the troposphere. Both gases play important roles in stratospheric ozone depletion [e.g. *Wofsy et al.*, 1975; *McElroy et al.*, 1986; *Mellouki et al.*, 1992]. Unlike anthropogenically-produced chlorofluorocarbons and halons, CH_3Br and CH_3Cl have both anthropogenic and natural sources [e.g. *Kurylo et al.*, 1999]. While the roles of bromine and chlorine in stratospheric ozone loss have been well documented, the atmospheric budgets of CH_3Br and CH_3Cl have large uncertainties, with the current estimates of known sinks greatly outweighing the known sources [*Kurylo et al.*, 1999]. Potential explanations for this imbalance include the existence of large unidentified source(s), underestimates of currently identified sources, and/or overestimated sinks. There is a clear need for additional constraints on their respective budgets. Stable isotopes have been suggested as a useful tool for providing such constraints [*McCauley et al.*, 1999]. Quantification of carbon isotope compositions of CH_3Br and CH_3Cl from various

sources, and the isotopic fractionations associated with loss mechanisms are needed to test the viability of this approach. Here we present stable carbon isotope and flux measurements of CH_3Br and CH_3Cl from a southern California coastal marsh. Coastal salt marshes have recently been identified as a large natural source of CH_3Br and CH_3Cl and are estimated to represent approximately 5 to 15% of the total source strength for both compounds [*Rhew et al.*, 2000].

2.   Experiment

2.1.   Sampling

[3]   Fluxes and carbon isotopic compositions of emitted CH_3Br and CH_3Cl were measured at three separate sites at the Mission Bay Marsh (32° 47′N, 117° 13′W), San Diego, California, on three days during the 1999 and 2000 growing seasons. The predominant vascular plant species covering the soil surface ($\sim80-90\%$ of the canopy cover) at these upper-middle marsh sites was the succulent halophyte, *Batis maritima* (saltwort). In a previous salt marsh study, the largest emissions of CH_3Br and CH_3Cl were associated with this vegetation type [*Rhew et al.*, 2000]. These compounds appeared to emanate from the plants or their associated microflora rather than from the soils or algae [*Rhew et al.*, 2000]. Fluxes were measured using a two-component, all-aluminum, dark, static flux chamber that covers a surface area of 1 m^2 and encloses a volume of 850 liters. Whole air samples were drawn from the chamber and stored in previously evacuated 6-liter fused-silica-lined stainless steel canisters. On June 30, 1999, three daytime flux chamber experiments to study CH_3Br and CH_3Cl fluxes and isotopic compositions were carried out at one site (Site C), with each experiment including samples at 1 and 15 minutes after closure of the chamber. Over a 24-hour period between July 18 and 19, 2000, seven additional flux chamber experiments were carried out at each of two other sites (Site A and B), with each experiment including samples at 1 and 20 minutes after closure, and additional 15-liter samples taken at 40 minutes after closure for isotopic measurements. The first three experiments at Site B were compromised by a poor seal between the chamber lid and base, which was corrected for the subsequent measurements. For both the 1999 and 2000 experiments, high tides occurred at approximately noon and 22:00 local time, during which time the sites were inundated with several cm of seawater. In the 2000 experiments, the surface of Sites A and B were drained of seawater during the afternoon low tide.

[4]   Ambient air temperatures ranged from 20°C at dawn to 27°C at midday in the 1999 study, and from 18°C during the night to 31°C at midday in the 2000 study. The associated relative humidities ranged from 73% to 55% in the 1999 study and from 98% to 29% in the 2000 study. Chamber temperatures were

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moderated using external reflective insulation, holding chamber temperatures within 3°C of ambient air temperatures. In the Site A experiments, a cooling unit with chilled water pumped through an internal radiator was also used, holding the chamber temperature within 1°C of ambient air temperatures.

2.2. Concentration and Flux Measurements

[5] CH_3Br and CH_3Cl concentrations were measured at the Scripps Institution of Oceanography (SIO) by capillary gas chromatography with cryogenic preconcentration and electron capture detection [*Miller*, 1998; *Miller et al.*, 1998] with oxygen-doping to enhance the sensitivity to these compounds. [*Grimsrud and Miller*, 1978]. At least two 80 cm^3 sub-samples from each flask were measured, utilizing less than 5% of the sample gas in the flasks. The relative analytical precisions typically ranged from 0.2 to 2%. Calibration curves were constructed with a suite of synthetic primary standards prepared at SIO, and the resultant sample concentrations have an estimated accuracy better than 5%. The detection limit on the instrument for these compounds was well below ambient concentrations (<10 ppt for CH_3Br, <550 ppt for CH_3Cl). Several high-concentration samples from the 2000 season were diluted with ultra-high purity synthetic air N_2-O_2 mixtures in order to improve the accuracy of the concentration measurements.

[6] For each chamber experiment, fluxes were quantified by plotting the molar ratio versus time, applying a linear fit to the data, and multiplying the slope by the number of moles of air in the chamber. Measurement uncertainties in chamber temperature, pressure, and volume yield small errors in the flux calculations. An additional uncertainty which is not quantified involves the use of only two chamber air measurements to derive fluxes, but the high precision of measurements and the relatively short enclosure time help to mitigate this problem.

2.3. Carbon Isotope Measurements

[7] Isotopic measurements were carried out at the Lawrence Berkeley National Laboratory (LBNL). After the concentration measurements, the remainder of the air samples in the 6-liter canisters were used for carbon isotope measurements. The additional 15-liter canisters were used for carbon isotope measurements only. CH_3Br and CH_3Cl were extracted using a preconcentration system coupled to a gas chromatograph (Figure 1). Samples from each canister were drawn through the pre-concentration system at a flow of 0.4 L min^{-1} using a diaphragm pump and were trapped in a 1/4-inch diameter chilled glass trap packed with glass beads. To avoid oxygen condensation, the pre-concentration trap was placed in nitrogen vapor above liquid nitrogen at
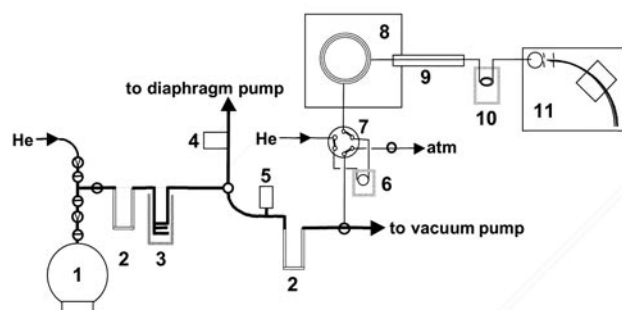
Figure 1. Instrumental configuration: 1. Sample canister; 2. Magnesium perchlorate and Ascarite II traps; 3. Glass coil packed with glass beads used for initial preconcentration; 4. Flow controller; 5. Vacuum gauge; 6. Silcosteel trap for cryofocusing sample; 7. 6-port valve for loading trap and then injecting samples; 8. Gas chromatograph; 9. Combustion reactor; 10. Water trap; 11. Isotope ratio mass spectrometer.
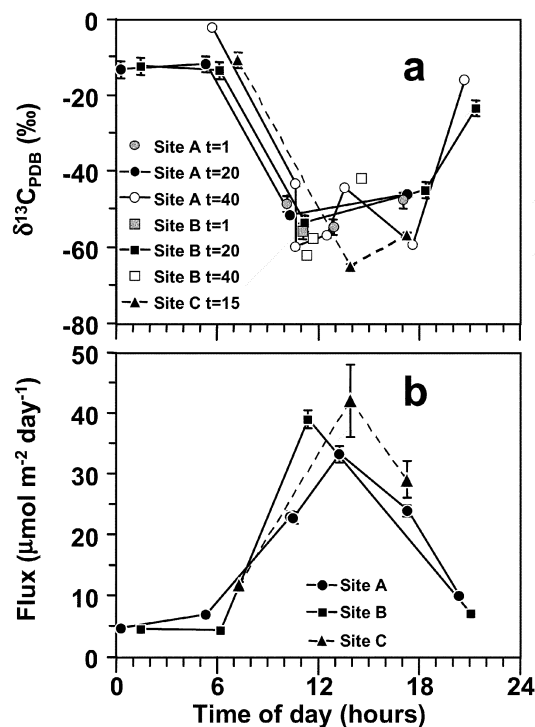
Figure 2. (a) $\delta^{13}C$ of CH_3Br ($\pm 1\sigma$ based on sample size) emitted from the salt marsh plant *Batis maritima*. (b) Associated variation of CH_3Br fluxes ($\pm 1\sigma$). Samples were taken in June 1999 and July 2000 from flux chambers in a salt marsh (Mission Bay, San Diego). Data are plotted as a function of time of day.

approximately −165°C. By warming in a hot water bath at ∼50°C and flushing the glass trap with ultra-pure helium, the pre-concentrated sample is transferred to a 0.5 mm diameter stainless steel loop placed in liquid nitrogen. Water and CO_2 were removed using magnesium perchlorate and Ascarite II (sodium hydroxide coated non-fibrous silicate) traps during the sample transfer. Samples were injected into the gas chromatograph (Hewlett Packard 6890 GC) by switching the 6-port valve and heating the loop with hot water at ∼50°C. Gases were separated chromatographically on a Supelco Supel-Q PLOT fused silica capillary column (30 m × 0.32 mm). Effluent from the GC column was transferred through a combustion furnace to convert the methyl halide carbon to CO_2, a cryogenic trap to remove water, and an isotope ratio mass spectrometer (Micromass, IsoPrime) to determine the isotopic composition. This method is similar to other methods described in the literature for measuring carbon isotopes of a variety of volatile organic compounds in air [*Rudolph et al.*, 1997; *Tsunogai et al.*, 1999].

[8] Stable carbon isotope ratios are expressed in the conventional δ-notation in parts per mil (‰) relative to the Peedee Belemnite (PDB) standard:

$$\delta^{13}C = \left[\left(^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{standard}\right)\big/\left(^{13}C/^{12}C_{standard}\right)\right] 1000$$

(1)

[9] Analytical precision was estimated by injecting different quantities of CH_3Br diluted in air into the GC using known volume loops connected to the 6-port valve (Figure 1). Repeated injections of a CH_3Br standard (Sigma Aldrich) yielded values of −54.0 ±
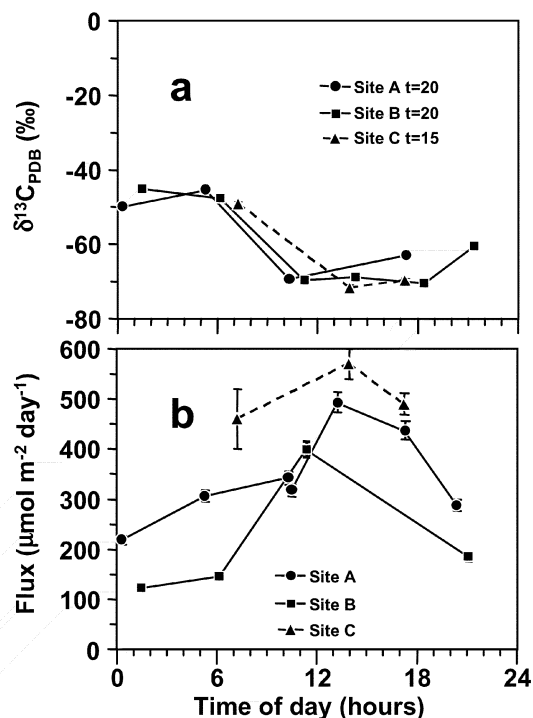
Figure 3. (a) δ^{13}C of CH$_3$Cl ($\pm 1\sigma$ based on sample size) emitted from the salt marsh plant *Batis maritima*. (b) Associated variation of CH$_3$Cl fluxes ($\pm 1\sigma$). Samples were taken in June 1999 and July 2000 from flux chambers in a salt marsh (Mission Bay, San Diego).

0.5‰ (1σ; $n = 13$) for standard sizes containing between 32 and 214 ng of carbon and -52.8 ± 3.6‰ (1σ; $n = 9$) for standards containing 1.3 ng of carbon. A different CH$_3$Br standard (Matheson) yielded a value of -62.9 ± 2‰ (1σ; $n = 21$) for standards containing between 3 and 20 ng of carbon. Precision decreased with decreasing sample size. Less than 3 ng of carbon was not useful for this experiment and defined the detection limit as 3 ng of carbon with precision of ± 2‰. Absolute calibration of the δ^{13}C in CO$_2$ produced from the combustion of CH$_3$Cl and CH$_3$Br was done by analyzing the CO$_2$ reference gas on the isotope ratio mass spectrometer (IRMS) before each sample was analyzed. The CO$_2$ reference gas was calibrated against National Institute of Standards and Technology (NIST) CO$_2$ standards RM 8562 δ^{13}C = -3.76‰, RM 8563 δ^{13}C = -41.56‰ and RM 8564 δ^{13}C = -10.45‰. Thus absolute accuracy of these measurements was limited by the precision when analyzing small samples rather than by accuracy of our method of standardization.

[10] Determination of the δ^{13}C value of CH$_3$Cl and CH$_3$Br emitted in the experiments must take into account the atmospheric background enclosed in the flux chamber. One minute after the closure of the flux chamber ($t = 1$), background CH$_3$Cl constituted approximately 5 to 30% of the sample and had higher δ^{13}C values than at $t = 20$. These values are not reported here because the atmospheric background for CH$_3$Cl was too large to clearly identify the emission signature. Twenty minutes after the closure of the flux chamber ($t = 20$), the CH$_3$Cl atmospheric background represents less than 0.5% of the total sample; therefore at this time, the δ^{13}C values are indicative of the emission signature. Measurements of δ^{13}C of CH$_3$Br were generally not possible at 1 minute after closure of the flux chamber due to its relatively low concentration ($\sim$120–2200 ppt) in the chamber. Simultaneous isotopic analyses of CH$_3$Cl and CH$_3$Br for samples taken at 40 minutes were not possible because the CH$_3$Cl samples with more than 400 ng of carbon were outside the range of linear response for the isotope ratio mass spectrometer.

3. Results and Discussion

[11] The two sites sampled in July 2000 had similar diurnal CH$_3$Br fluxes with midday fluxes differing by $\sim$15% (Figure 2b). CH$_3$Cl fluxes measured in the two sample sites also showed a similar diurnal trend with values differing by $\sim$20% at midday (Figure 3b). The lowest fluxes of CH$_3$Br (5 μmol m^{-2} d^{-1}) and CH$_3$Cl (150–300 μmol m^{-2} d^{-1}) occurred at night, and the largest fluxes occurred around midday (40 μmol m^{-2} d^{-1} for CH$_3$Br and 400–550 μmol m^{-2} d^{-1} for CH$_3$Cl). The fluxes measured in 1999 showed a similar daytime variation and had maxima fluxes which were roughly 10% larger (Figures 2 and 3).

[12] A strong diurnal variation in δ^{13}C of CH$_3$Br and CH$_3$Cl was also observed (Figure 2a and Figure 3a). The maximum δ^{13}C values of CH$_3$Br (-12‰ to -2‰) and CH$_3$Cl (-50‰ to -45‰) occurred at night and corresponded to the lowest fluxes (Figures 2 and 3). The minimum δ^{13}C values of CH$_3$Br (-65‰ to -59‰) and CH$_3$Cl (-71‰ to -69‰) were observed around midday and coincided with the highest emissions and ambient temperature. Hence, the relatively lighter halomethane molecules were preferentially emitted during times of maximum emission from the salt marsh (Figures 2 and 3). The mean daily δ^{13}C values of CH$_3$Br and CH$_3$Cl emitted from the salt marsh, weighted by the emission rates, were -43‰ $\pm$ 2 and -62‰ $\pm$ 3 respectively. At least two hypotheses are compatible with our observations of the diurnal δ^{13}C variation of CH$_3$Br and CH$_3$Cl emissions:

  a) It is possible that the isotopic composition of the carbon source (presumably the methyl donor S-adenosyl-L-methionine, or
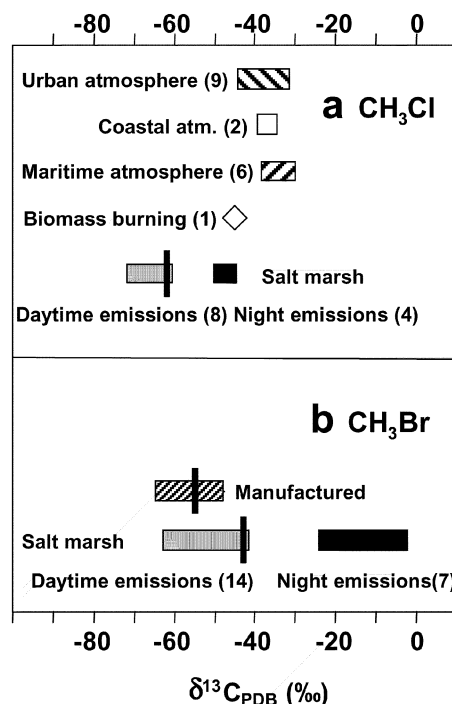

Figure 4. (a) δ^{13}C comparison between net CH$_3$Cl emitted from the salt marsh and CH$_3$Cl in different urban, coastal, and maritime atmospheres after *Tsunogai et al.* [1999] and from C-3 plant biomass burning after *Rudolph et al.* [1997]. (b) δ^{13}C comparison between net CH$_3$Br emitted from the salt marsh and industrially manufactured CH$_3$Br after *McCauley et al.* [1999]. Vertical bars indicate the weighted mean δ^{13}C values of salt marsh emissions and manufactured CH$_3$Br. Number of samples is indicated in parentheses.

SAM) may have a diurnal cycle, with enrichment in ^{13}C at night leading to methyl halide emissions also being enriched in ^{13}C. This could explain the similar δ^{13}C signatures of CH$_3$Br and CH$_3$Cl during the day but would need to be coupled with an additional process to explain the different δ^{13}C values during the night, and might suggest that the loss process fractionates CH$_3$Br more than CH$_3$Cl.

b) A variation of the ratio of production to consumption of the methyl halides could explain the differences in the nightime δ^{13}C values. During nighttime, net production of CH$_3$Br and CH$_3$Cl is lower and the isotopic ratio becomes enriched in ^{13}C, which could be due to consumption of CH$_3$Br and CH$_3$Cl. During degradation reactions, bonds containing the heavier isotopes have higher dissociation energies than those containing light isotopes. Therefore, ^{12}C-Br bonds in CH$_3$Br and ^{12}C$-$Cl bonds in CH$_3$Cl are preferentially broken before ^{13}C$-$Br bonds and ^{13}C$-$Cl respectively [e.g. *Bill et al.*, 2001, *Miller et al.*, 2001]. This would leave the remaining methyl halide enriched in ^{13}C.

[13] Few measurements of methyl halide δ^{13}C have been reported in the literature. δ^{13}C of atmospheric CH$_3$Cl from maritime, coastal and urban areas were reported by *Tsunogai et al.* [1999] and δ^{13}C of CH$_3$Cl from C-3 plant biomass burning were reported by *Rudolph et al.* [1997]. Our measurements of δ^{13}C of daytime CH$_3$Cl emissions from the salt marsh (−62‰ to −71‰) are lower than the published atmospheric measurements (−30.5‰ to −44.1‰) or the biomass burning measurements (−45‰), whereas δ^{13}C values of nighttime emissions (−45‰ to −49‰) overlap with the δ^{13}C of biomass burning emissions (Figure 4a). Salt marsh emissions had a weighted mean δ^{13}C of −62‰, approximately 17‰ lower than biomass burning.

[14] A comparison of δ^{13}C values of CH$_3$Br with atmospheric values is not possible because the δ^{13}C of tropospheric CH$_3$Br has not yet been measured. Based on our salt marsh measurements, the mean δ^{13}C from this source is −43‰. The only published δ^{13}C values for CH$_3$Br sources are from industrially manufactured CH$_3$Br at −54.4‰ [*McCauley et al.*, 1999], approximately 11‰ lower than salt marsh emissions (Figure 4b). However δ^{13}C of industrially produced CH$_3$Br does not necessarily reflect the releases from fumigated fields, crops or structures. Processes such as hydrolysis or biodegradation by bacteria are usually associated with strong kinetic isotope effects [*Miller et al.*, 2001], and would likely increase the δ^{13}C of the fraction of CH$_3$Br applied during fumigation that is released to the atmosphere.

4. Conclusions

[15] We found that CH$_3$Br and CH$_3$Cl emissions from the vascular plant *Batis maritima* in coastal salt marshes had strong diurnal variations in fluxes and δ^{13}C values. The largest fluxes of CH$_3$Br and CH$_3$Cl were associated with the lowest δ^{13}C values. Salt marsh emissions of CH$_3$Br and CH$_3$Cl had a daily weighted mean δ^{13}C of −43‰ and −62‰, significantly different from other known source signatures, suggesting that carbon isotopes may provide an effective tool for constraining the global atmospheric budgets of CH$_3$Br and CH$_3$Cl. However, this data set is limited and more measurements are needed to determine global source δ^{13}C signatures for natural plant emissions of methyl halides.

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