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Carbon isotope fractionation of methyl bromide during agricultural soil fumigations

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Abstract. The isotopic composition of methyl bromide (CH_3Br) has been suggested to be a potentially useful tracer for constraining the global CH_3Br budget. In order to determine the carbon isotopic composition of CH_3Br emitted from the most significant anthropogenic application (pre-plant fumigation) we directly measured the $\delta^{13}C$ of CH_3Br released during commercial fumigation. We also measured the isotopic fractionation associated with degradation in agricultural soil under typical field fumigation conditions. The isotopic composition of CH_3Br collected in soil several hours after injection of the fumigant was –44.5‰ and this value increased to –20.7‰ over the following three days. The mean kinetic isotope effect (KIE) associated with degradation of CH_3Br in agricultural soil (12‰) was smaller than the reported value for methylotrophic bacterial strain IMB-1, isolated from previously fumigated agricultural soil, but was similar to methylotrophic bacterial strain CC495, isolated from a pristine forest litter zone. Using this fractionation associated with the degradation of CH_3Br in agricultural soil and the mean $\delta^{13}C$ of the industrially manufactured CH_3Br (–54.4‰), we calculate that the agricultural soil fumigation source has a carbon isotope signature that ranges from –52.8‰ to –42.0‰. Roughly 65% of industrially manufactured CH_3Br is used for field fumigations. The remaining 35% is used for structural and post-harvest fumigations with a minor amount used during industrial chemical manufacturing. Assuming that the structural and post-harvest fumigation sources of CH_3Br are emitted without substantial fractionation, we calculate that the $\delta^{13}C$ of anthropogenically emitted CH_3Br ranges from –53.2‰ to –47.5‰.

Introduction

Methyl bromide (CH_3Br) is a trace gas that constitutes the largest source of bromine atoms to the stratosphere and plays an important role in stratospheric ozone depletion. While the role of bromine in stratospheric ozone loss has been well documented, the current understanding of CH_3Br sources suffers from major uncertainties. Unlike chlorofluorocarbons, CH_3Br is released by

both natural and anthropogenic processes. The largest natural sources appear to be biological production in the oceans and inorganic production during biomass burning followed by coastal salt marsh emissions (Kurylo et al. 1999; Rhew et al. 2000). The anthropogenic sources are dominated by agricultural fumigation. The magnitude of the anthropogenic source is known, but only to within 50%, despite the efforts made to quantify emissions from agricultural soil fumigation (e.g. Yagi et al. 1993; Yagi et al. 1995; Majewski et al. 1995; Yates et al. 1996a; Yates et al. 1996b). Identification of the carbon isotope composition of CH_3Br from various sources and the fractionation occurring during degradation (sinks) should enable us to construct an isotope mass balance and therefore to constrain the budget of CH_3Br (McCauley et al. 1999). Previous studies demonstrated that isotopic fractionations are associated with uptake mechanisms of CH_3Br in which the atmospheric reservoir becomes enriched in heavy isotopes (Kalin et al. 2001; Miller et al. 2001). Recently published isotopic data show that at least some natural sources emit isotopically light CH_3Br. For instance, salt marsh emission had a mean $\delta^{13}C$ value of $\approx$ –43‰ with large diurnal variability (Bill et al. 2002).

Industrially manufactured CH_3Br has a mean $\delta^{13}C$ value of –54.4‰ (McCauley et al. 1999). However only a fraction of that anthropogenic CH_3Br enters the atmosphere and therefore the released CH_3Br could be isotopically fractionated (McCauley et al. 1999). To address this issue, we measured the $\delta^{13}C$ of CH_3Br emitted during fumigation of agricultural fields. We also determined the mean kinetic isotope effect (KIE) associated with degradation in agricultural soils in order to better determine the average carbon isotope signature from anthropogenic sources.

Experiment

Sampling

The field fumigation experiment was conducted at the Monterey Bay Academy field site (Santa Cruz County, California, U.S.A.) between 18 and 21 September, 2001. The soil is a sandy loam (Elder) with low organic carbon (<1%) and neutral pH (6.8, Shaun Baesman pers. comm.). Fumigant [57% CH_3Br and 43% Chloropicrin (CCl_3NO_2) ratio by weight] was applied by a commercial applicator at a rate of 20 g m^{-2} at 30 cm depth using a tractor. The field was immediately covered with a 0.025 cm thick polyethylene tarp and remained covered for 6 days. Samples were collected from beneath the tarp for CH_3Br concentration and carbon isotope composition using a 0.6 cm O.D. $\times$ 100 cm length stainless steel tube. At each sampling location, the tube was pushed progressively deeper in order to terminate at selected depths

above, at, or below the soil surface. Placing a solid rod inside the tube during insertion prevented plugging of the bottom of the tube with soil. The rod was removed during sampling. Soil gases were collected in evacuated serum bottles sealed with rubbers stoppers. No sample replicates were collected. Gas samples were analyzed for concentration within several hours and for isotope composition within one week. The flux of CH_3Br emitted to the atmosphere through the polyethylene tarps during fumigation was determined on the day following the injection of fumigant using static flux chambers (volume = 21 liters, Miller et al. 2001) placed over the tarps. Chamber headspace samples were collected for determination of concentration using 1 cm^3 glass syringes and for determination of isotopic composition using evacuated 57 cm^3 serum bottles.

Analytical

Concentrations of CH_3Br were determined in the field using ECD gas chromatography (3 m length × 0.3 cm O.D. Krytox column, Alltech; Miller et al. 1997). Carrier (P-5, 5% methane, balance argon) flow was 25 cm^3 min^{-1}.

Isotopic measurements were carried out at the E.O. Lawrence Berkeley National Laboratory, Earth Sciences Division, Berkeley, U.S.A. CH_3Br samples were injected into a gas chromatograph (Hewlett Packard 6890 GC) with a 6-port valve equipped with 15 to 100-microliter loops. CH_3Br was separated chromatographically using a Supelco Supel-Q™ PLOT fused silica capillary column (30 m length × 0.32 mm I.D.). Effluent from the GC column was transferred through a combustion furnace to convert the CH_3Br to CO_2 (at 850 °C: $CH_3Br + 3CuO \rightarrow H_2O + HBr + CO_2 + 3Cu$). A cryogenic trap was used to remove water. The carbon isotope composition of CO_2 was determined using an isotope ratio mass spectrometer (IsoPrime, Micromass). Relative stable isotope ratios of carbon ($^{13}C/^{12}C$) were determined directly for CO_2 in the mass spectrometer by measuring masses 44, 45 and 46.

The isotopic composition of carbon is reported in per mil deviations relative to the Peedee Belemnite (PDB) standard in the conventional δ-notation:

$$\delta^{13}C = [(^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{standard})/(^{13}C/^{12}C_{standard})] \times 1000 \qquad (1)$$

The precision of the $\delta^{13}C$ measurements was tested by repeatedly injecting different quantities of a commercial CH_3Br (Sigma Aldrich). Repeat measurements of CH_3Br standards containing between 12 and 55 nanograms of carbon yielded values of –54.04 ± 0.51‰ (1σ, n = 18). The absolute calibration of the isotope ratio mass spectrometer (IRMS) was done by determination of mass ratios 44/45 and 44/46 on CO_2 reference gas. The CO_2

reference gas used for IRMS calibration was calibrated against National Institute of Standards and Technology (NIST) CO_2 standards RM 8562 ($\delta^{13}C$ = –3.76‰), RM 8563 ($\delta^{13}C$ = –41.56‰), and RM 8564 ($\delta^{13}C$ = –10.45‰). During each measurement of organic compound, CO_2 reference gas was introduced into the mass spectrometer. Thus, CO_2 produced from the combustion of methyl halides is compared to the calibration value for every sample individually. For these reasons we take the standard deviation (1 sigma) of the precision measurement as the accuracy.

Isotope fractionation is expressed as a kinetic isotope effect (KIE), defined for carbon as the ratio (r_c) of the rate constant for reaction with $^{12}CH_3Br$ to that for reaction with $^{13}CH_3Br$. KIE can be deduced by:

$$\delta^{13}C_t = 1000[(1/r_c) - 1] \ln(M/M_o) + \delta^{13}C_i \quad (2)$$

where $\delta^{13}C_t$ and $\delta^{13}C_i$ are the delta values of the remaining and initial CH_3Br, and M and Mo are the remaining and the initial concentrations of CH_3Br. The KIE is determined from the slope of the line defined by equation (2) by plotting $\delta^{13}C_t$ versus ln(M/Mo) (Coleman et al. 1981). In this paper KIE is reported in per mil notation and is defined by:

$$\epsilon = 1000(r_c - 1) \quad (3)$$

Results and discussion

An initial CH_3Br concentration of 2.5% was measured in the space between the soil and tarp a few hours after injection of fumigant (Figure 1(A)). Soil concentration of CH_3Br was lower (1.7%) at 20 cm, near the depth of injection. Initial CH_3Br concentration was lowest (0.4%) below the depth of injection at 40 cm. CH_3Br concentrations over the following days decreased exponentially. Note that, on any sampling date, concentrations of CH_3Br were similar at the three shallowest depths (0 and 20 cm depth and in the space between the soil and tarp) whereas concentrations were lower throughout the experiment at 40 cm depth.

An increase in $\delta^{13}C$ of CH_3Br with time was observed following the injection of soil fumigant (Figure 1(B)). The most negative values of $\delta^{13}C$ (–44.5‰ to –42.5‰) were measured a few hours after fumigant injection. Values of $\delta^{13}C$ increased linearly over the three days of measurement with a final value of –20.7‰. As degradation in the soil progressed, the soil became enriched in heavier CH_3Br isotopes and the CH_3Br emitted to the atmosphere became increasingly heavier compared to the industrial product applied.

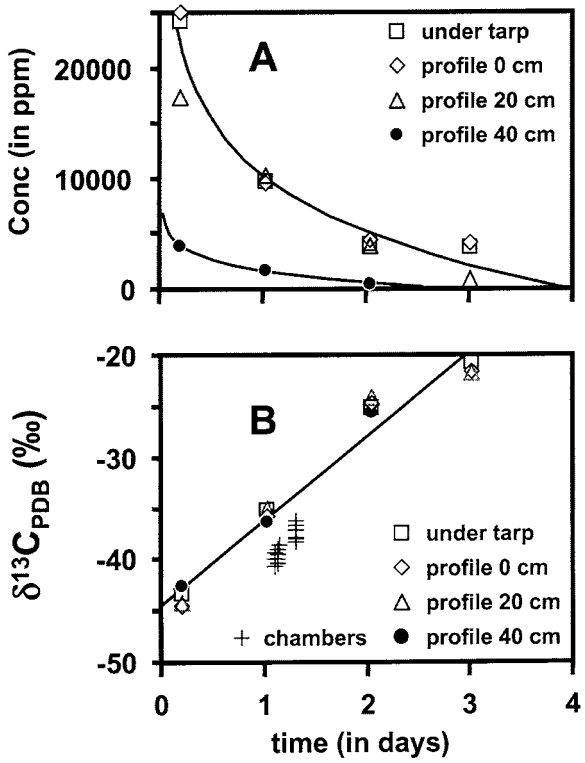

Figure 1. (A) Concentration and (B) carbon isotope composition of CH_3Br measured in agricultural soil over 3 days at different depths. Soils were fumigated at day 0. Values of $\delta^{13}C$ for CH_3Br collected in flux chambers are reported for two chamber deployments ($n = 6$ chambers each) after 1 day. The concentration of CH_3Br at 40 cm was below the detection limit on day 3.

Samples of CH_3Br emitted were collected one day after fumigant injection using flux chambers placed over the tarp. Flux data showed similarly increasing trends of $\delta^{13}C$ as in soil profiles but with slightly more negative $\delta^{13}C$ values ($\sim$5‰) indicating that isotope transport through the polyethylene tarp may be strongly influenced by diffusion (Figure 1(B)) as previously suggest by Yates et al. (1996b). Despite the variation of concentration with depth in the soil, the carbon isotope composition was constant with depth and changed only with the progress of the reaction (Figure 2). These observations suggest that transport of CH_3Br between 40-cm depth and the soil-tarp interface is dominated by advection. Differential diffusion of ^{12}C and ^{13}C methyl bromide would result in a gradient in the $\delta^{13}C$ of CH_3Br between the different depths, which was not observed.

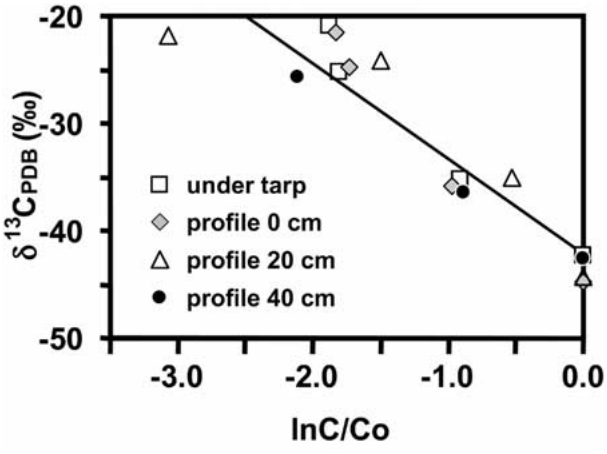

Figure 2. Carbon isotope composition of CH_3Br versus the relative change in concentration over 3 days at different depths. Co is the initial concentration at each depth. The regression line fits all data points.

The KIE we calculated from field measurements represents an apparent KIE that includes all processes of CH_3Br loss or degradation which simultaneously participate in CH_3Br consumption. Based on samples taken from under the tarp at 0 cm and at 20 cm depth, the KIE in our field fumigation experiment ranged from 10.9‰ to 13.4‰ with a mean value of 11.6‰. This KIE is lower than those associated with oxidation of CH_3Br by methylotrophic bacteria IMB-1 (66‰ ± 6 and 72‰ ± 3 for experiments at low and high cell density, respectively) and by the marine strain MB2 (63‰ ± 5 and 57‰ ± 5) but is closer to methylotrophic bacterial strain CC495 (4‰ ± 2) reported by Miller et al. (2001) (Figure 3). This observation is compatible with a biotic degradation process in which bacteria induce similar fractionation as bacterial strain CC495 and which could be accompanied by loss of CH_3Br through the tarp by diffusion as suggested by $\delta^{13}C$ measurements from flux chambers. The apparent KIE may also be influenced by other processes that remove CH_3Br and which fractionate carbon isotopes. For example, chemical degradation of CH_3Br via hydrolysis or exchange with soil organic matter may play a role if these processes are significant sinks or their KIE's are large. However, previous field and laboratory experiments suggest that bacterial degradation of CH_3Br in agricultural soils is more important that chemical degradation (Miller et al. 1997).

Knowledge of the KIE for any process that removes CH_3Br during agricultural field fumigations can help determine the impact that fumigations have upon the atmospheric budget of CH_3Br with the following caveats: (1) The process is well distributed in soils that are fumigated, (2) the KIE is constant

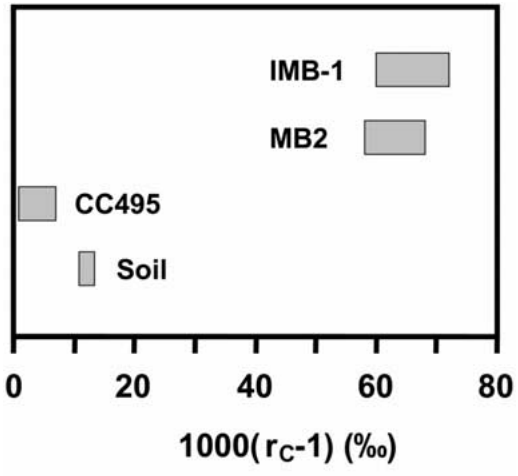

Figure 3. KIE of CH_3Br degradation in agricultural soil compared with experimental KIEs determined for different bacterial strains at 26 °C, after Miller et al. (2001).

over a range of physical conditions, such as temperature and soil moisture, and (3) if the process is bacterial, that the KIE is representative of the strains of bacteria likely to be encountered in fumigated soils. If these conditions are met, then Equation 2 or Figure 4 may be employed to estimate the contribution of field fumigations to the global atmospheric burden of CH_3Br. Several research groups have estimated, with different methods, that between 35 and 86% of the CH_3Br applied to agricultural fields is emitted to the atmosphere (Yagi et al. 1993; Yagi et al. 1995; Majewski et al. 1995; Yates et al. 1996a; Yates et al. 1996b). This range was attributed to differences in climatic conditions, differences in polyethylene tarp permeability and variability of degradation rates below some of the flux chambers (Yates et al. 1996a). Based on the weighted average $\delta^{13}C$ of industrially manufactured CH_3Br (–54.4‰, McCauley et al. 1999) and the range of estimates of the percent of CH_3Br emitted, the resulting $\delta^{13}C$ of CH_3Br released to the atmosphere can be estimated to range from –52.8‰ to –42.0‰ (Figure 4). The lower limit of the isotopic signature of CH_3Br emissions from fumigated fields (more negative $\delta^{13}C$ values) corresponds to situations characterized by higher permeability tarps and/or low rates of biodegradation whereas the higher (less negative) value of the source signature would be associated with low permeability tarps and/or higher biodegradation rates.

The $\delta^{13}C$ source signature of CH_3Br emitted during agricultural fumigation can be compared with the only published $\delta^{13}C$ value of natural CH_3Br emissions, which is from salt marsh plants (Bill et al. 2002). Salt marsh emis-

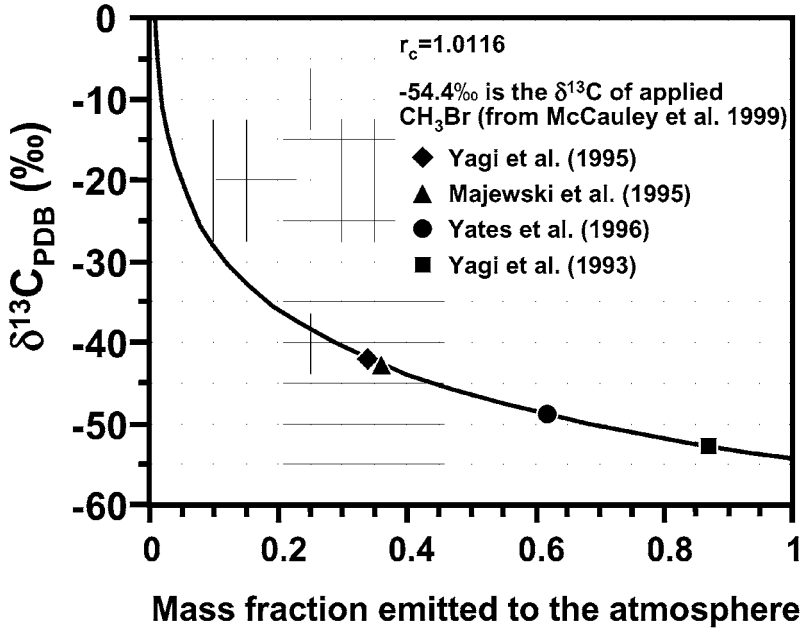

Figure 4. $\delta^{13}C$ values of CH_3Br emitted to the atmosphere versus mass fraction of CH_3Br emitted to the atmosphere during field fumigations. Symbols represent estimates of CH_3Br Emission to the atmosphere during fumigation (from Yagi et al. 1993; Yagi et al. 1995; Majewski et al. 1995; Yates et al. 1996a; Yates et al. 1996b). The curve was constructed using equation (2), the mean KIE measured in the agricultural soil (ϵ = 11.6‰), and –54.4‰ as the global mean $\delta^{13}C$ value of industrially manufactured CH_3Br, after McCauley et al. (1999).

sions have a mean $\delta^{13}C$ value of –43‰ ± 2, which falls within the range of $\delta^{13}C$ values calculated for the CH_3Br signature of the fumigation soil source.

The isotopic signature of the total manufactured CH_3Br emitted to the atmosphere can be estimated by calculating a weighted mean of the $\delta^{13}C$ from soil fumigation and other anthropogenic sources. The fumigation of harvested crops and structures releases 14.1 ± 2.1 kton y^{-1} and since the release rate of the applied CH_3Br approaches 100%, these emissions should have a mean $\delta^{13}C$ close to the industrially manufactured CH_3Br (–54.4‰) (Kurylo et al. 1999; McCauley et al. 1999). By considering the upper estimate for CH_3Br emitted to the atmosphere during soil fumigation (46.1 kton y^{-1}, corresponding to 87% of the CH_3Br applied which has a $\delta^{13}C$ of –52.8‰, Figure 4) and the fumigation of harvested crops and structures (16.4 kton y^{-1}, which represent 26.2% of the total manufactured CH_3Br emitted to the atmosphere), we estimate the lower limit for the isotopic composition of anthropogenically emitted CH_3Br to be –53.2‰. The upper limit for the isotopic composition of anthropogenically emitted CH_3Br would be –47.5‰ based on the assumption

that 18 kton y^{-1} of CH_3Br are emitted to the atmosphere during soil fumigation and 12.2 kton y^{-1} are released during fumigation of harvested crops and structures. Thus, we estimate that the $\delta^{13}C$ value of anthropogenically emitted CH_3Br ranges from –53.2‰ to –47.5‰. The uncertainty in determining a mean value of emitted CH_3Br derives mainly from the large range in estimated CH_3Br emissions to the atmosphere during fumigation (35% to 86%; Yagi et al. 1993; Yagi et al. 1995).

Conclusions

CH_3Br degradation in agricultural soil is associated with a significant increase of $\delta^{13}C$ values over the course of fumigation. During fumigation, the carbon isotope composition of CH_3Br in the soil is constant with depth. Despite the fact that concentration varies with depth, $\delta^{13}C$ values change only with the progress of CH_3Br degradation. The KIE calculated for CH_3Br degradation in the soil is consistent with degradation controlled by bacterial activity which could be associated with loss beneath the tarp. Mechanisms such as hydrolysis or exchange with soil organic matter would be important only if they are important sinks or have large KIEs.

The isotopic composition of the CH_3Br field fumigation source ranges from –52.8‰ to –42.0‰. This range in $\delta^{13}C$ overlaps the range of salt marsh plant source values (–43‰ ± 2) suggesting that, at the present time, it is difficult to separate these two sources by carbon isotope measurements. For the future, experiments that refine the estimates of $\delta^{13}C$ source signatures will determine whether this isotopic approach is likely to provide useful information for constraining the global atmospheric budget of CH_3Br.

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