Emission of Methyl Bromide from Biomass Burning

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Bromine is, per atom, far more efficient than chlorine in destroying stratospheric ozone, and methyl bromide is the single largest source of stratospheric bromine. The two main previously known sources of this compound are emissions from the ocean and from the compound's use as an agricultural pesticide. Laboratory biomass combustion experiments showed that methyl bromide was emitted in the smoke from various fuels tested. Methyl bromide was also found in smoke plumes from wildfires in savannas, chaparral, and boreal forest. Global emissions of methyl bromide from biomass burning are estimated to be in the range of 10 to 50 gigagrams per year, which is comparable to the amount produced by ocean emission and pesticide use and represents a major contribution (≈30 percent) to the stratospheric bromine budget.

The depletion of the Earth's stratospheric ozone layer is cause for great concern. The main reason for the recent reductions in stratospheric ozone is the increased catalytic conversion of O_3 to O_2 by the ClO radical. The precursors of the ClO radical are the long-lived chlorofluorocarbons (CFCs). These compounds have been and still are commonly used as refrigerants, propellants, and solvents. According to the Montreal Protocol of 1987, the use of these compounds has been restricted, and with time CFCs will be phased out completely. Shorter lived compounds such as methyl chloride (CH_3Cl) have also been drawn into the ozone layer discussion (*1*). Recently, much attention has been focused on methyl bromide (CH_3Br), because bromine is known to be much more efficient on a per atom basis than chlorine in breaking down ozone (by a factor of ≈40) (*2*) and may be responsible at present for ≈20% of the Antarctic ozone depletion. A recent assessment (*3*) attributed 5 to 10% of the current global loss of stratospheric ozone to CH_3Br alone. In order to evaluate the possibilities for limiting this threat, it is essential to determine the sizes of the natural and anthropogenic sources of CH_3Br.

Methyl bromide is believed to be the main reservoir of atmospheric bromine, and an average atmospheric concentration of about 9 to 13 parts per trillion has been found (*3*, *4*), which corresponds to a global burden of 150 to 210 Gg (1 Gg = 10^9 g). On the basis of this burden and an estimated atmospheric lifetime of 2 years (*3*, *4*), a total global CH_3Br source of 75 to 105 Gg/year is obtained. If deposition to land and vegetation surfaces provides an additional sink for CH_3Br, as has been suggested in recent reports (*1*, *3*), the lifetime of CH_3Br could be as short as 1 year, which requires a source strength of 150 to 210 Gg/year. Production by marine plankton is one natural source of CH_3Br, and saturation ratios of 140 to 180% in surface seawater have been reported (*4*). The ocean source is estimated to produce 35 Gg/year, with an uncertainty of as much as ± 50% (*4*). Another source is the use of CH_3Br as a pesticide; 50 to 80% of the total quantity of CH_3Br used in this way is believed to escape to the atmosphere (*3*, *5*). On the basis of sales and production statistics, the Methyl Bromide Industry Panel estimated these emissions for 1990 to be 33 Gg out of a total use of 66 Gg. Given the uncertainties in these calculations, a range of 20 to 60 Gg/year for anthropogenic emissions appears reasonable (*3*).

Because these two sources alone can barely account for the low end of the range of the global source estimates of 75 to 210 Gg/year, there may be one or more additional sources. It has long been known that CH_3Cl is found in smoke plumes from biomass burning (*6*), and the global CH_3Cl flux from this source has been estimated to be 1.8 Tg/year (1 Tg = 10^{12} g), with an uncertainty of a factor of 2 (0.9 to 3.6 Tg/year). In two independent papers, it has recently been speculated that biomass burning could also be a source of atmospheric CH_3Br (*4*, *7*). This suggestion was confirmed by preliminary measurements done on smoke from vegetation fires (*8*).

We conducted biomass burning experiments in a combustion laboratory (*9*, *10*) under controlled conditions. During the fires, the CO and CO_2 concentrations in the smoke were measured continuously. Samples of stack gas were collected in evacuated stainless steel canisters. In the field, samples were collected in similar canisters from aircraft flying over active fires. The canister samples were analyzed, without any drying or precleaning step, by capillary gas chromatography combined with mass spectrometry (*11*).

The CO and CO_2 concentrations in smoke gas samples from a savanna grass fire are shown in Fig. 1A. The grass sample for the experiment was collected in Kruger National Park in South Africa. At the start of the fire, combustion is very efficient, CO_2 emission is high, CO concentration is low, and the fire burns with an open flame (flaming phase). After passing across the fire bed, the open flame disappears. At the end of the flaming phase, the CO_2 concentration drops and the CO concentration rises (smoldering phase). During the less efficient smoldering combustion, a large number of organic compounds are formed (*10*, *12*). The CH_3Br and CH_3Cl data from the same fire are shown in Fig. 1B. The CH_3Cl shows a maximum during smoldering, as expected. More surprising is that CH_3Br shows two maxima, one during the flaming phase and one during the smoldering. In slower burning fires where there is little or no open flame, CH_3Br and CH_3Cl both show a maximum only during the smoldering phase. From a total of 50 smoke samples obtained from experimental burns of savanna grass and similar fuels, we calculated the molar emission ratio for CH_3Br relative to CO_2 as follows:

$$\frac{\Delta CH_3Br}{\Delta CO_2} = \frac{[(CH_3Br)_{Smoke}] - [(CH_3Br)_{Ambient}]}{[(CO_2)_{Smoke}] - [(CO_2)_{Ambient}]}$$

The emission ratio thus calculated ranged from 0.044×10^{-6} to 0.77×10^{-6}, with an average of 0.29×10^{-6}. This value compares well to the emission ratio found by Manö *et al.* (*8*) for California chaparral fires (0.65×10^{-6}). A similar value (0.46

Table 1. Molar emission ratios for CH_3Br and CH_3Cl (–, not determined).

Origin of data	Burn phase	Emission ratio	
		$\Delta CH_3Br/\Delta CO_2$	$\Delta CH_3Br/\Delta CH_3Cl$
Laboratory fires	Flaming	0.12×10^{-6}	–
	Smoldering	0.39×10^{-6}	–
	Total fire	0.29×10^{-6}	3.4×10^{-3}
Chaparral fires	Total fire	0.65×10^{-6}	10.3×10^{-3}
African savanna fires (*13*)	Total fire	0.46×10^{-6}	8.4×10^{-3}
Boreal forest fires	Total fire	1.30×10^{-6}	19.0×10^{-3}

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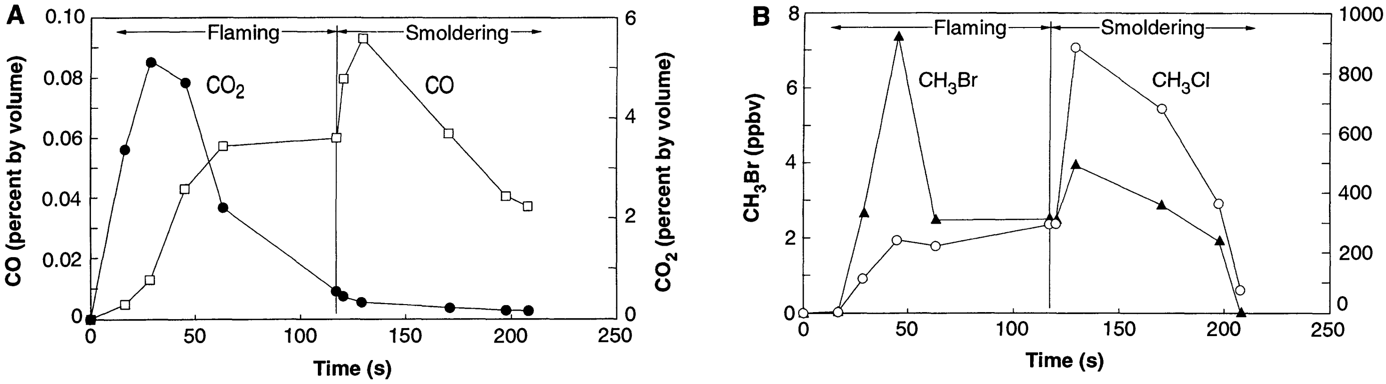

Fig. 1. Data taken during the laboratory burn of South African savanna grass. (**A**) Variation of CO and CO_2 concentrations with time in the smoke produced by the burn (the points represent individual measurements from the sample canisters and have been interconnected to guide the eye). The flaming phase is characterized by high CO_2 concentrations. Later, during smoldering, CO reaches a maximum. (**B**) Variation of CH_3Br and CH_3Cl concentrations with time in the smoke gas during the same experiment.

Table 2. Emission estimates for CH_3Br from biomass burning. For the calculations of these estimates, we assumed that the ranges indicated represent 95% confidence limits and used standard error propagation calculations.

Molar emission ratio relative to CO_2	0.4×10^{-6} to 1.3×10^{-6}
Emission estimate for CO_2 from biomass burning	2.5 to 4.5 Pg of C $year^{-1}$
Emission estimate for CH_3Br based on CO_2 data	9 to 37 Gg/year
Molar emission ratio relative to CH_3Cl	6×10^{-3} to 9×10^{-3}
Emission estimate for CH_3Cl from biomass burning	0.65 to 2.6 Tg/year
Emission estimate for CH_3Br based on CH_3Cl data	22 to 50 Gg/year

$\times 10^{-6}$) was derived for savanna fires from the $\Delta CH_3Br/\Delta CO$ ratio of 8.5×10^{-6} measured during the SAFARI-92 experiment in Kruger Park (*13*) and the $\Delta CO/\Delta CO_2$ ratio of 0.055 that is typical of savanna fires worldwide. We also analyzed samples from a boreal forest fire near Krasnoyarsk, Siberia, and found higher emission ratios for CH_3Br (0.11×10^{-6} to 3.1×10^{-6}) and CH_3Cl (8×10^{-6} to 140×10^{-6}) than those found in emissions from grass, savanna, and chaparral fires. Forest fires usually have a lower combustion efficiency than grass fires, and therefore a larger fraction of smoldering compounds is formed. Table 1 lists the emission ratios for CH_3Br from laboratory and field fires during various burning phases and shows that the emission ratios of the various laboratory and field fires fall in a relatively narrow range.

We used CH_3Cl measurements made on the same samples used for CH_3Br determinations to derive a CH_3Br/CH_3Cl emission ratio. In spite of more complex behavior of CH_3Br during the combustion process, the emission ratios from our laboratory fires, from field measurements in California (*8*), from the South African savanna (*13*), and from the boreal forest (*14*) all fall in a relatively narrow range around 1 mole percent (mol%) (Table 1). This ratio is similar to the Br/Cl ratios found in plants (0.1 to 1 mol%) (*15*).

To estimate the global emission of CH_3Br from biomass burning, we used these emission factors together with published estimates of pyrogenic emission of CO_2 and CH_3Cl (*12*). In Table 2, we give estimated ranges for the mean values of the emission ratios of CH_3Br/CO_2 and CH_3Br/CH_3Cl as well as emission estimates based on these ranges. Obviously, these values have a high degree of uncertainty, given the small data set now available. However, the reasonably close agreement between measurements taken in the laboratory and at various field locations, and between measurements made by different laboratories, strongly supports the validity of these estimates. When these emission ratios are multiplied with the global rates of emission from biomass burning of CO_2 [2.5 to 4.5 Pg of carbon per year (1 Pg = 10^{15} g)] (*12*) and CH_3Cl (0.65 to 2.6 Tg of chlorine per year) (*12*), we obtain estimated pyrogenic emissions of CH_3Br ranging from 9 to 37 and from 22 to 50 Gg/year, respectively. We therefore suggest that the pyrogenic source of CH_3Br falls in the range of 10 to 50 Gg/year (or 10 to 50% of the total source strength), with a best estimate of 30 Gg/year, and that the pyrogenic source is of the same order of magnitude as the other major sources of CH_3Br, ocean emission and pesticide use. It is evident that pyrogenic emissions of CH_3Br and CH_3Cl are important components of the stratospheric halogen budget. During preindustrial times, biomass burning must have ranked next to marine emission of these gases as the dominant source of halogens released to the stratosphere.

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11. The analytical column used was a 50-m Cp-Sil-5 (Chrompack) with an internal diameter of 0.32 mm and a film thickness of 1.2 μm. A gas sample (5 to 10 ml) was cryofocused onto the column before the analysis. With the mass spectrometer set to selected ion monitoring mode, the following masses were recorded: 50 ($CH_3{}^{35}Cl$), 52 ($CH_3{}^{37}Cl$), 94 ($CH_3{}^{79}Br$), and 96 ($CH_3{}^{81}Br$). For calibration, a permeation source for CH_3Cl was used, as a permeation device for CH_3Br was not available. The response for CH_3Br relative to CH_3Cl was determined by dilution of a small volume of 100% CH_3Br and CH_3Cl in a 100-liter Tedlar bag (Chrompack International, Middelburg, Netherlands). The detection limit was about 0.5 ppb and the precision of the method is within ±10%.
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Retention of Solar Helium and Neon in IDPs in Deep Sea Sediment

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It was recently proposed that subduction of interplanetary dust particles (IDPs) contained in deep sea sediments could have introduced substantial solar helium and neon to the Earth's mantle. However, it is not certain if IDPs would retain solar noble gases during subduction. A diffusion experiment that examined He and Ne in IDPs in a magnetic separate from Pacific Ocean sediments showed that He and Ne would be lost from IDPs within 3 years at 500°C, and possibly within 10^5 years at 200°C, which suggests that they would be lost from subducting slabs at shallow depths.

An important recent discovery in noble gas geochemistry is the presence of a solar-like Ne component ($^{20}Ne/^{22}Ne \sim 13$) in mantle-derived samples such as midocean ridge basalts (*1–3*), Loihi and Kilauea basalts (*3, 4*) and gases (*1*), xenoliths (*5*), diamonds (*6*), CO_2-well gases (*7*), and geothermal gases (*8*). The observation of solar-like Ne in such a wide variety of sample types suggests that it is a characteristic noble gas signature of the mantle.

Interplanetary dust particles are rich in solar He and Ne and characterized by high $^3He/^4He$ and $^{20}Ne/^{22}Ne$ ratios of $\sim 10^{-4}$ and 12 to 13, respectively (*9, 10*), and deep sea sediments, especially their magnetic fractions, contain solar He and Ne associated with IDPs (*11–18*). On the basis of these observations, Allègre *et al.* (*19*) attributed solar-like Ne in the mantle, and Anderson (*20*) attributed solar-like Ne and ^3He in the mantle, to subduction of sediments carrying IDPs rich in extraterrestrial (ET) noble gases. Because some deep sea sediments subduct into the mantle, He and Ne in IDPs may contribute to the present noble gas signature in the mantle if the fallout rate of IDPs is high enough to account for the present noble gas signature in the mantle and if IDPs can retain solar He and Ne during subduction.

Allègre *et al.* (*19*) and Anderson (*20*) estimated the fluxes of ET noble gases (^3He and Ne) to deep sea sediment and compared them with the outgassing fluxes from the mantle. As Anderson discussed (*20*), the ET flux of noble gases to deep sea sediment must be estimated on the basis of noble gas data (*12*) instead of refractory element data (*21*), because noble gases would be lost from large IDP grains ($\gtrsim 50$ μm) by frictional heating on entering the atmosphere (*22, 23*). The flux of ^3He to the sea floor that is associated with IDPs is estimated to be 8×10^3 cm^3/year (*12*), whereas the outgassing flux of ^3He from the mantle is calculated to be $\sim 3 \times 10^6$ cm^3/year (*20*)—a value two to three orders of magnitude greater. A similar result was obtained for Ne by Allègre *et al.* (*19*), though their preference seems to be for a larger IDP flux and for nearly balanced fluxes of ET Ne in and out of the present mantle. Although it is not necessary to assume a complete balance between the above two fluxes (*19, 20*), the present ET flux is apparently too small to make an important contribution to the present noble gas composition of the mantle (*20*). Hence, the contribution of IDP flux in the past must be considered (*19, 20*). However, it is not certain whether the fallout rate of IDPs in the past was high enough to account for the present Ne (and ^3He) in the mantle.

The second question is whether IDPs can retain solar He and Ne during subduction. Amari and Ozima (*16*) conducted a diffusion experiment for He in magnetic separates from deep sea sediments and obtained the activation energy of 17 kcal/mol (71 kJ/mol). Matsuda *et al.* (*18*) also conducted a stepwise heating experiment for He and Ne in a magnetic separate (and its HCl-treated samples) and determined the D/a^2 values (D is the diffusion coefficient and a is the radius of the grains) at 1000°C to be (6 to 8) $\times 10^{-5}$ s^{-1} for ^4He and (6 to 7) $\times 10^{-6}$ s^{-1} for ^{20}Ne. Activation energies were not given in their paper, supposedly because of the small number of data points. Allègre *et al.* (*19*) and Anderson (*20*) argue that IDPs are rather retentive of solar noble gases, because some solar noble gases were retained in IDPs even above 1000°C in the stepwise heating experiments (*16, 18*). However, heating time for noble gas extraction in such experiments was only ~1 hour, and the results cannot be directly applied to the geological process at subduction zones.

To measure more precisely the retention of solar He and Ne in IDP grains, I conducted a diffusion experiment. A magnetic fraction was separated from a Pacific Ocean sediment (92SAD01) dredged at 9°30′ to 9°31′N, 174°17′W, and at a depth of 5737 to 5810 m, by the ship *Hakurei-maru No. 2* (Geological Survey of Japan). About 300 g of wet sediment, corresponding to about 85 g of dry sediment, was sieved and grains of <74 μm in size were separated out (*24*). About 200 mg of magnetic material was collected from this fine sediment by use of hand magnets. The collected sample was magnetite with some impurities of silicate grains containing inclusions of magnetic minerals. Two samples, MG1-2 (60.10 mg) and MG1-3 (106.95 mg), were prepared from this magnetic fraction for noble gas analysis. Each sample was wrapped with platinum foil to avoid possible reactions between magnetite and the molybdenum crucible (*25*). Stepwise heating was applied to extract noble gases from the samples; MG1-2 was heated from 600° to 1400°C with 200°C steps and MG1-3 was heated from 500° to 1300°C with 100°C steps. The temperature was maintained for 2 hours at each step. The samples were finally melted at 1600°C to extract the remaining gases. Helium and neon were separated with the use of a cryogenic refrigerator and analyzed separately with a sector-type mass spectrometer (*3*). Hot blanks for ^4He and ^{20}Ne were $\sim 5 \times 10^{-9}$ cm^3 [standard temperature and pressure (STP)] and $\sim 7 \times 10^{-11}$ cm^3 (STP), respectively, for the temperatures from 500° to 1600°C, and hot blank corrections (though negligible for most of the temperature fractions) were applied in the calculation of the amounts of gases released from the samples.

The observed concentrations of ^4He and ^{20}Ne were $\sim 9 \times 10^{-6}$ cm^3/g and $\sim 8 \times 10^{-8}$ cm^3/g, and the observed $^3He/^4He$ and $^{20}Ne/^{22}Ne$ ratios were (2.3 to 2.6) $\times 10^{-4}$ and 11.2 to 12.6, respectively (Table 1), which are characteristic of noble gas signatures of IDPs (*14, 16–18*). Atmospheric contamination was negligible for He, judging from the high $^3He/^4He$ ratios (>100 times the atmospheric ratio of 1.4×10^{-6}) and the high concentration of He. Contamination was minor for Ne, judging from the high $^{20}Ne/^{22}Ne$ ratios as compared with the atmospheric ratio (9.8). However, to avoid the possible contribution of atmospheric Ne, I used the following definition of excess ^{20}Ne in the diffusion calculation

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