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Vertical distribution of methyl bromide over Hyderabad, India

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ABSTRACT

A vertical distribution profile of methyl bromide (CH_3Br), obtained from the samples collected at Hyderabad (17.5°N, 78.6°E) during a balloon flight conducted on 9 April 1990, is presented. Its mixing ratio varies from 8 pptv at 10 km to 0.5 pptv at 25 km altitude. It shows a sharp decrease above the tropopause. CH_3Br is the major source of bromine radicals in the atmosphere in the 13 to 27 km height region. Halon 1211 (CF_2BrCl) is the second major contributor of Br radicals in the 10 to 25 km height region while Halon 1301 (CF_3Br) is the major source of these radicals only above 25 km. The measured CH_3Br profile agrees fairly well with the available results from 1-D and 2-D model computations.

1. Introduction

Methyl bromide (CH_3Br) is an important source of bromine (Br) radical in the earth's atmosphere. It has a relatively short lifetime ranging from 1.2 to 2 years (Singh et al., 1993; Khalil et al., 1993). The loss of this gas is mainly due to reaction with OH in the troposphere and photolysis in the stratosphere, which produces free Br radicals. These Br radicals react with ozone and form BrO radicals. Both Br and BrO are in equilibrium. The BrO_x (Br and BrO) radicals, inspite of their much lower concentrations compared to the ClO_x radicals, play an important role in the loss of stratospheric ozone, since bromine is about 40 to 100 times more effective than chlorine in ozone destruction (Yung et al., 1980). Loss of ozone due to bromine in the Antarctic region is estimated to be around 30% (Solomon, 1990; Salawitch et al., 1990). Although the oceans are believed to be the major sources of this gas, recent observations suggest anthropogenic sources as well (Khalil et al., 1993). Methyl bromide is used as a soil, grain and space fumigant, it is also emitted from automobile exhaust and biomass burning. Man-made sources of CH_3Br are estimated to be about 35% of the total budget (Singh and Kanakidou, 1993). High concentration of this gas has been observed in urban areas. Also a positive latitudinal gradient, from the southern hemisphere to the northern hemisphere, has been observed in CH_3Br mixing ratio (Penkett et al., 1985). Recent CH_3Br data show an increase of 0.3 ± 0.1 pptv (parts per trillion, 10^{12}, by volume)/yr during the last four years (Khalil et al., 1993). Data on the vertical distribution, which is necessary to study the influence of this species in the ozone chemistry, is very limited. In fact, there are no data available on the vertical distribution of CH_3Br, except for a preliminary result by Fabian et al. (1981). This paper presents vertical distribution profile of CH_3Br, obtained from the analysis of the air samples collected in the altitude region of 10 to 35 km during a balloonborne cryosampler experiment conducted over India.

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2. Experimental programme

Under a joint programme between the Max Planck Institute for Aeronomy (MPAE), Lindau, Germany and Physical Research Laboratory (PRL), Ahmedabad, India, a balloon flight, carrying a composite payload of a cryogenic air sampler of MPAE and a suntracking multichannel photometer of PRL was conducted from Hyderabad (17.5°N, 78.6°E), India on 9 April 1990. Air samples were collected at 15 different levels in the altitude region of 10 to 35 km, during both ascent and the slow, valve-controlled descent of the balloon. The samples were analysed after about five months using a gas chromatograph (Dani 6800) coupled with a quadrupole mass spectrometer (Balzers QMG511) at MPAE. A 4-m glass column packed with OV-101 on chromosorb WHP together with mass selection on mass spectrometer was used for separation and detection. Methyl bromide was detected at m/e 95. This gas together with many other halogenated gases was separated clearly. The sample volume required for detection of these gases ranged from 0.7 l to 1.5 l. The detection limit for CH_3Br was about 0.2 pptv with sample volume of 1.5 l. Each sample was analysed twice or thrice. The repeatability of these measurements was about $\pm 10\%$. Some of the available samples, collected from 1987 balloon flights at Hyderabad and Southern France (43.7°N, 0.25°W), were also analysed for this gas. These results did not show any deterioration of the samples for the gases under study, beyond the analysis error.

Absolute calibration made at MPAE using a static dilution technique gives a value of 8.0 pptv for tropospheric samples with an uncertainty of $\pm 20\%$. Previous surface measurements of CH_3Br reported by Singh (1977), Singh et al. (1979, 1983), Rasmussen and Khalil (1980, 1984), Penkett et al. (1985), Khalil et al. (1993), Berg et al. (1984), Cicerone et al. (1988) and Bottenheim et al. (1990) are shown in Fig. 1. Measurements made in the recent years give an average tropospheric concentration of about 10 pptv and some are even less, about 8 pptv.

3. Vertical distribution of CH_3Br

The vertical profile obtained from the analyses of air samples collected from Hyderabad, India, on 9 April 1990, shows a nearly constant mixing ratio of about 8 pptv upto about 20 km, but above this height it decreases sharply to about 1.5 pptv at 23.6 km and 0.5 pptv at 25 km (Fig. 2). CH_3Br

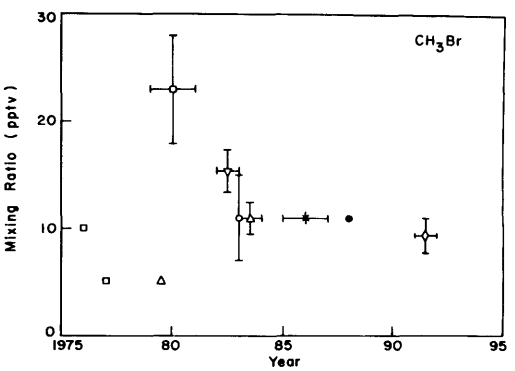

Fig. 1. Surface measurements of CH_3Br at different locations and periods: □, Singh (1977); □, Singh et al. (1979, 1983); △, Rasmussen and Khalil (1980, 1984); ⋈, Penkett et al. (1985); ⋄, Berg et al. (1984); ⋈, Cicerone et al. (1988); ●, Bottenheim et al. (1990); ⋄, Khalil et al. (1993).

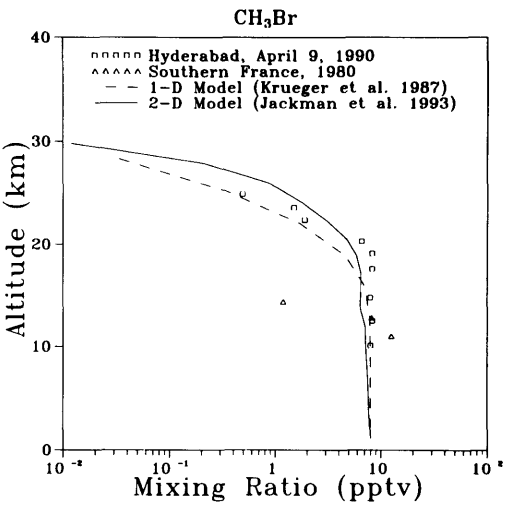

Fig. 2. Vertical distribution of CH_3Br obtained at Hyderabad (17.5°N) and southern France (43.7°N). These are compared with model computations. The Hyderabad profile and the model profiles are normalised for mean tropospheric mixing ratio of 8 pptv.

could not be detected in samples collected above 27 km altitudes due to the sensitivity limitation of the system. The only earlier measurement from Southern France reported by Fabian et al. (1981) showed a very sharp fall at a much lower altitude region of 12–15 km. The Hyderabad profile is in reasonably good agreement with the results of the 1-D model of Krueger et al. (1987) and the 2-D model of Jackman and Douglass (1993). The model mixing ratios are normalised to our absolute value of 8.0 pptv to study the vertical distribution of CH_3Br. The observed fall in the mixing ratio above 20 km is sharper than that calculated by the 2-D model. The tropopause for this flight was recorded at 17 km.

A calculation has been made to estimate the production of bromine radicals from the three main bromine containing gases which have been measured from the samples of the same balloon flight. Bromoform ($CHBr_3$), with a tropospheric mixing ratio of about 3–6 pptv and life time of the order of months (Cicerone et al., 1988), may contribute to the production of Br radicals at lower heights. However, its vertical distribution profile is not obtained so far. Fig. 3 shows observed concentrations of Halon 1211 (CF_2BrCl), Halon 1301 (CF_3Br) and CH_3Br for the balloon flight conducted from Hyderabad on 9 April 1990. The vertical distribution profile of Halon 1211 and Halon 1301 are taken from Singh et al. (1994). The tropospheric mixing ratio of CH_3Br is the highest (8 pptv), while the mixing ratios of Halons 1211 and 1301 are 3 pptv and 1.7 pptv respectively. In the stratosphere CH_3Br decreases most sharply followed by Halon 1211. Photodissociation rates are calculated for these three gases for a solar zenith angle of 45° using absorption cross-sections given by Gillotay et al. (1989). CH_3Br also reacts with OH, which is the main loss process below about 10 km. The production rate (P_{i^z}) of bromine radicals due to photodissociation at different altitudes (z) for a particular compound (i) is given by the following expression:

$$P_{i^z} = J_{i^z} \cdot n_{i^z},$$

where J_{i^z} is the photodissociation rate at height z and n_{i^z} is the number density of ith gas. Fig. 4 shows the Br production rates for the 3 gases above 10 km height. Above 13 km height, photodissociation of CH_3Br produces more free bromine than dissociation of the halons, peaking at 20 km height. The production rate of Br radicals at this peak is 0.6 mole cm^{-3} s^{-1}. Halon 1211 is also a major source of Br in the 10 to 25 km height

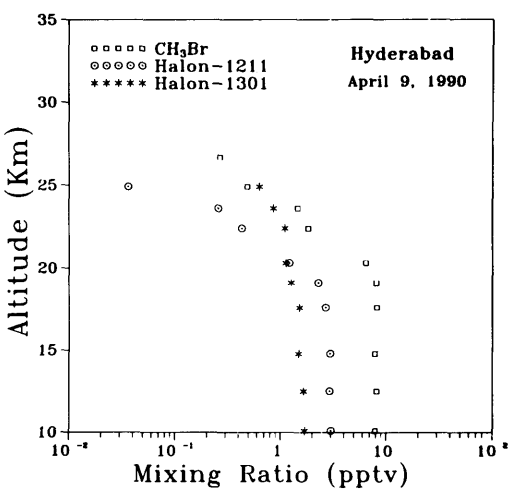

Fig. 3. Vertical mixing ratio profiles of three bromine containing gases (CH_3Br, Halon-1211 and Halon-1301) measured at Hyderabad, India on 9 April 1990.

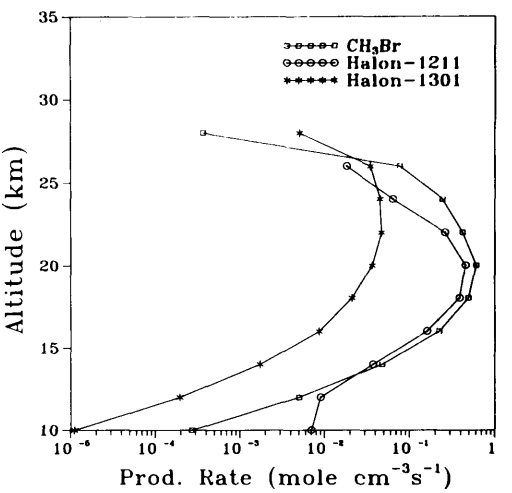

Fig. 4. Calculated production rate of bromine radicals due to phodissociation at different stratospheric altitudes for CH_3Br, Halon-1211 and Halon-1301.

region. However, bromine production from the photodissociation of Halon 1211 is lower than that due to CH_3Br photodissociation with a peak value of 0.45 mole cm^{-3} s^{-1} at 20 km. Halon 1301 is the predominant source of free bromine only above 25 km.

4. Summary

Vertical distribution profile of methyl bromide (CH_3Br) upto 27 km altitude is obtained from the samples collected using a balloonborne cryogenic air sampler from Hyderabad. The observed tropospheric mixing ratio is 8 pptv while at 25 km height it is only 0.5 pptv showing a sharp decrease above the tropopause which was recorded at 17 km height. Production of Br radicals have been estimated for 45° solar zenith angle for CH_3Br, Halon 1211 and Halon 1301. CH_3Br is the major source of these radicals in the height region of 13 to 27 km with a peak production of 0.6 mole cm^{-3} s^{-1} at 20 km. Halon 1211 also contributes significantly in this height range but Br production is 25% less than that of CH_3Br at 20 km. Halon 1301 is the major source of Br radicals only above 25 km.

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