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1990 VERTICAL DISTRIBUTION OF TWO IMPORTANT HALONS – F-12B1 AND F-13B1 – IN THE TROPICS

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ABSTRACT

The first vertical profiles of F–12B1 and F–13B1 had been obtained in the tropical troposphere and stratosphere by us in 1987 [Singh et al., 1988, 1988a]. The measurement of these substances responsible for almost the entire anthropogenic contribution to the stratospheric BrO_x budget is important in the tropics, as tropical upwelling provides their injection along with that of other pollutants, into the stratosphere. To ascertain the trends of these distributions and foster the data, the 1987 experiment was repeated in April 1990. Like 1987, the MPAE cryogenic whole air sampler was launched on a balloon from Hyderabad, India (17.5°N), and 14 samples were colleded between 10 and 35 km altitude. The results obtained by means of GC and GC-MS analyses showed that the atmospheric abundance of both F–12B1 and F–13B1 is increasing at a fast rate, respectively by about 15% and 10% per year. From 1987 to 1990, F–12B1 and F–13B1 tropospheric mixing ratios have been growing from 1.2 and 1.3 ppt to 1.8 and 1.7 ppt, respectively. The vertical profiles will be discussed.

1. INTRODUCTION

The atmospheric composition of bromine species is still largely unknown, although much progress has been made since the original suggestion was put forth in mid seventies that bromine might play a role in atmospheric photochemistry [Wofsy et al., 1975]. The injection of these species into the atmosphere is due to natural as well as anthropogenic sources. Hardly any inorganic bromine has been measured so far in the troposphere by species specific methods, and only measurements of total inorganic bromine are available. Very few good measurements have been made to date on stratospheric bromine amounts, but several model calculations have attempted to estimate the stratospheric bromine concentrations from the available values of known sources like halons, CH_3Br and $CH\ Br_3$.

In 1988 a comprehensive review of the bromine level in the atmosphere was made on the basis of its earlier measurements [Salawitch et al., 1988]. It was concluded that the total organic bromine source is between 6 and 20 pptv, with 3 pptv being the anthropogenic bromine gases of recent origin and the rest being methyl bromine and bromoform. The life time of CH_3Br in the troposphere is about one year, and 80% of the organic bromine would ultimately be converted into inorganic forms at about 20 km altitude. It was concluded from these facts that the total inorganic bromine reservoirs in the lower stratosphere should also be in the range of 6–20 pptv.

The main sources of anthroprogenic bromine loading in the lower stratosphere are identified as the emissions from two halons 1301 or CFC-13B1 ($CBrF_3$) and 1211 or CFC-12B1 ($CBrClF_2$), used mostly as indestructible and portable fire extinguishers in the electronic and computer industries as well as in military and high technology settings. Halon 2402 or CFC-24B2 ($CF_2Br\ CF_2Br$) and bromoform, being short lived, are expected hardly to contribute to the stratospheric bromine budget, although they are quite important in the troposphere. As fully

halogenated hydrocarbons, CFC-13B1 and CFC-12B1 have long lifetimes estimated to range between 72-107 and 12-18 ys respectively [Fabian, 1986; WMO, 1990]. Their only sink in the atmosphere is ultraviolet photolysis. As the absorption cross section of $CBrF_3$ is exceedingly small ($\sim 10^{-25}$ cm^2) beyond 290 nm, it undergoes barely any photodecomposition in the troposphere and is decomposed mainly in the stratosphere by UV radiation of 190–285 nm wavelengths. The tropospheric photodecomposition of $CBrClF_2$, which has relatively large cross sections ($\sim 10^{-22}$ cm^2) beyond 290 nm, cannot be completely ignored [Singh et al., 1988, 1989].

2. CURRENT STATUS OF THE MEASUREMENT

The tropospheric abundance of F-13B1 was first measured in 1979 as 0.7 pptv [Penkett et al., 1981]. Only a couple of northern mid-latitude and one tropical vertical profiles, all obtained by this group for both F-12B1 and F-13B1, have been reported thus far [Fabian et al., 1981, 1984; Lal et al., 1985; Singh et al., 1988]. The vertical distribution of these two halons in the tropics were first obtained from air samples collected over Hyderabad, India (17.5 N) in 1987. The significance of the tropical measurements are two fold: 1) They are the very first profiles of such trace gases in tropics; and 2) these two halons, along with other longlived pollutants, are injected into the stratosphere over these latitudes due to tropical upwelling. To augment the 1987 measurements and to foster the scanty data base with regard to the trace gas concentrations in the lower tropical stratosphere, air over Hyderabad has again been collected by using the MPAE neon cooled cryogenic whole air sampler in April 1990, and the vertical distribution of these halons alongwith over 20 other trace gases has been obtained.

3. RESULTS

The details with regards to the cryogenic sampler, balloon flights and GC-ECD and GC-MS analytical equipments used are similar as discussed in our earlier papers [Fabian et al., 1984; Borchers et al., 1987, Singh et al., 1988]. The major modification incorporated in this case is the use of capillary columns (DB–1) on either of the equipments using preconcentration and cryofocussing technique.

The 1990 profiles of these two halons given in Figs. 1 and 2 show more or less similar trend as obtained in 1987. The model simulations of the profiles for F-12B1, using the MPAE-1D model and the new emission data from Prather and Watson (1990), yield higher values when compared with the present measurements (Fig. 3). Whereas, for F-13B1, similar calculations yielded good agreement with measured values, when old emission data from Fabian (1988) were used (Fig. 4).

The volume mixing ratio in the free tropical troposphere (between 11 and 17 km) of F-12B1 and F-13B1 have

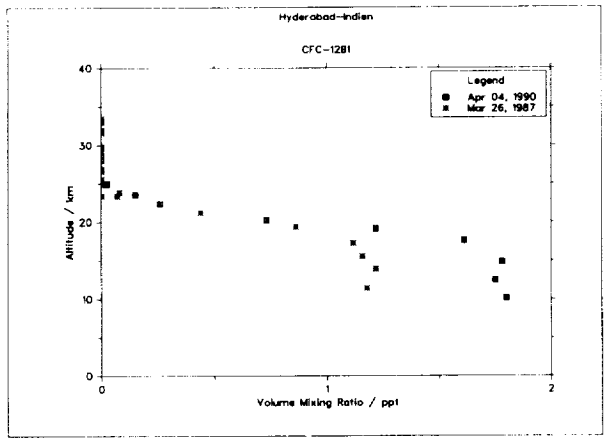

Fig. 1 1990 and 1987 vertical profiles of F–12B1 in the tropics. Please note that absolute values have been revised according to results of calibration procedures carried out after the Quadrennial Ozone Symposium.

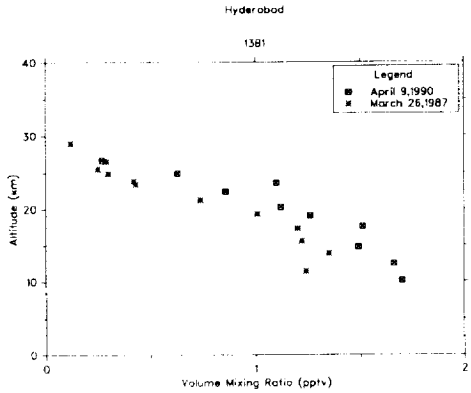

Fig. 2 1990 and 1987 vertical profiles of F–13B1 in the tropics.

been, respectively, estimated to be about 1.8 pptv and 1.7 pptv. This shows an increase per year of ~15% in F-12B1 and ~10% in F-13B1 concentrations. It may be emphasized that for ascertaining the growth rate of these halons, the air samples collected in 1987 and 1990 were analysed simultaneously in identical conditions. Our values are different from those projected in the IPCC (1990) Report to the extent that we measure both, the absolute volume mixing ratio and the growth rate, larger for F-12B1, whereas in the aforesaid report they are higher for F-13B1. Our results by part (F-13B1) are consistent with the totals of the emissions of 112,946 tonnes of F-12B1 and 48,377 tonnes of F-13B1 claimed accurate within 2 to 3% [McCulloch, 1992], measured values are lower for F-12B1.

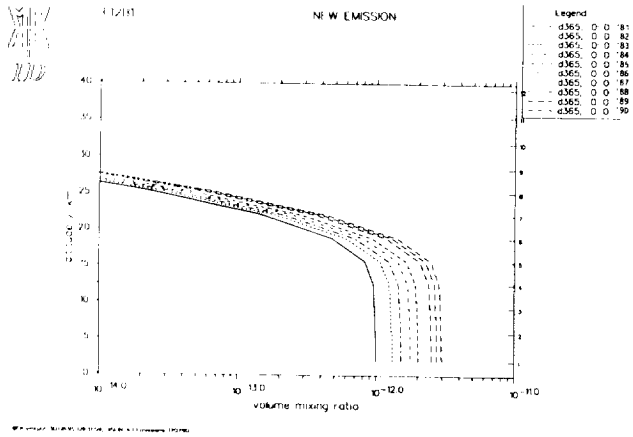

Fig. 3 Model profiles for F-12B1 using new emission data.

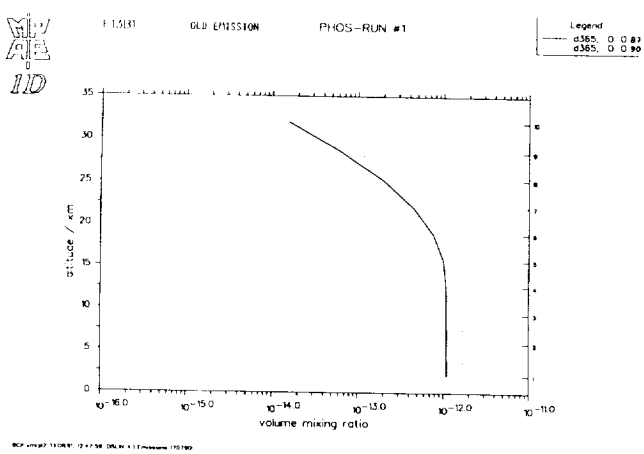

Fig. 4 Model profiles for F-13B1 using old emission data.

4. DISCUSSION

Shortly after the detection of the ozone hole, it was being contemplated that about 15–20 pptv of BrO_x in the Antarctic atmosphere should be sufficient to account for the springtime ozone destruction [Pyle and Farman, 1987; Singh, 1988]. But the current model simulations and calculations based on the various **in situ** measurements of ClO_x and BrO_x, OClO, N_2O, and several other species carried out during the NOZE and AOOE campaigns over Antarctica, strongly suggest that the role of bromine in the springtime polar ozone destruction is not so dominant as thought earlier [Brune et al., 1989; Solomon et al., 1989, 1990]. It is responsible for 10–30% of ozone depletion, and the remainder is credited to chlorine. Nevertheless bromine remains undoubtedly a potential ozone depleter and observations, although limited, indicate that bromine is ~40 times more effective than chlorine for ozone loss [Solomon and Albritton, 1992; Solomon et al., 1992]. Thus its man-made sources ought to be fully investigated and accounted for. Presently about one sixth of the total stratospheric bromine loading is supposedly due to F-12B1 and F-13B1, which are of entirely anthropogenic origin [Prather and Watson, 1990; Singh, 1992]. Further, these halons are potent greenhouse gases [Singh, 1989]. As emphasised earlier, several more measurements are necessary to establish conclusively the absolute abundance and the growth rate of these halons.

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