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Observed vertical profile of sulphur hexafluoride (SF_6) and its atmospheric applications

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Abstract. The vertical distribution of sulphur hexafluoride (SF_6) was measured during a balloon-borne cryogenic air sampler experiment conducted from Hyderabad (17.5^0N, 78.6^0E) on April 16, 1994, in the altitude region of about 8-37 km. The profile shows a faster decrease in its concentration in the region between the tropopause (~17 km) and about 27 km, which is known as the transition region. Above this region the decrease rate is almost an order of magnitude less than in the transition layer. These results indicate very little loss of SF_6 due to photochemistry in the stratosphere. Based on the reported increase rate of SF_6 mixing ratio at ground level and assuming that long-lived trace gases are transported to the stratosphere without any measurable loss from the troposphere through the equatorial tropopause, the age of stratospheric air is estimated to vary from 1±0.08 years near the tropopause to 4.26±0.17 years above the transition layer. Atmospheric lifetime of SF_6, inferred from the mixing ratio correlations with simultaneous measurements of N_2O, and CFC-12, is computed to be about 1937±432 years.

Introduction

Sulphur hexafluoride (SF_6) is emitted from the Earth's surface, purely due to anthropogenical activities, and is one of the most stable gases in the Earth's atmosphere, having a long atmospheric lifetime. There is almost no photochemical loss of SF_6 in the troposphere and lower stratosphere. Its major loss is considered to be the photodissociation by energetic Lyman α radiation at mesospheric heights [*Ravishankara et al.*, 1993]. Its long-term measurements showed a global mean abundance of 3.44 parts per trillion by volume (pptv) and a growth rate of 6.9%/year in 1994 [*Maiss et al.*, 1996]. SF_6 is considered to be a better dynamical tracer than the conventional ones such as CO_2, CF_4, and C_2F_6 [*Bischof et al.*, 1985; *Schmidt and Khedim*, 1991; *Harnisch et al.*, 1996], as its sources are solely anthropogenic, it has a high growth rate, and it is mostly emitted from the northern hemisphere. Recently, it has also been used as a tool for estimating the age of the stratospheric air [*Harnisch et al.*, 1996], which is useful in evaluating the ozone depletion potentials of various source gases [*Pollock et al*, 1992].

Sulphur hexafluoride is one of the most efficient greenhouse warming gases [*Ko et al.*, 1993], and since it has a high rate of increase in concentration and a long atmospheric lifetime, these combine to make SF_6 a possible candidate for future global warming. The atmospheric lifetime of SF_6 is still debated to a large extent; however, few attempts have been made to solve this problem [*Ravishankara et al.*, 1993; *Ko et al.*, 1993]. These uncertainties are probably due to the lack of information on reaction rates and photoabsorption cross sections. Proper estimation is needed for realistic evaluation of its impact on global change.

Here we describe the vertical distribution of SF_6, measured during a balloon-borne cryogenic air sampler experiment carried out on April 16, 1994, from Hyderabad (17.5^0N, 78.6^0E), India. This profile is used to calculate the age of the stratospheric air over an equatorial site and to estimate its atmospheric lifetime.

Experimental Procedure

A balloon carrying a cryogenic air sampler was launched on April 16, 1994, from Hyderabad (17.5^0N). Air samples were collected at 14 different altitudes in the

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height range of 8-37 km. Details of the cryosampler and the experiment conducted are described by *Lal et al.* [1996]. The samples are stored in the original sampling tubes without any transfer.

Air samples were analyzed at the Physical Research Laboratory (PRL), Ahmedabad, for SF_6 and various halogenated compounds, using a gas chromatograph equipped with an electron capture detector. About 80-100 mL of sample at STP was cryogenically (-196^{0}C) preconcentrated prior to injection onto the column head. Sulphur hexafluoride and various other CFCs are separated on a 4 m × 0.32 cm OD stainless steel column packed with PORASIL-L (80/100 mesh). The column temperature was varied from -50^{0}C to 200^{0}C during the analysis.

Reproducibility of these analyses was about 4% (at 99.7% confidence level) for SF_6 for samples from any altitude. The absolute concentrations are obtained by calibrating PRL working standard as well as a tropospheric sample with respect to a gravimetrically prepared standard [*Maiss et al.*, 1996] at the Institut für Umweltphysik, University of Heidelberg, Germany.

Results and Discussions

Measurement of the Vertical Profile

Vertical distribution of sulphur hexafluoride measured from the samples collected over Hyderabad (17.5^{0}N, 78.6^{0}E) during the April 16, 1994, balloon flight is shown in Figure 1. Volume mixing ratio of SF_6 decreases slowly from a tropospheric value of 3.18±0.006 (1σ) pptv at around 8 km to 3.05±0.005 (1σ) pptv near the tropopause (at 17.2 km). In the lower stratosphere its concentration decreases at a much faster rate (~0.06 pptv/km), attaining a value of 2.43±0.02 (1σ) pptv at around 27 km. However, the decrease rate (~0.01 pptv/km) is slower again in the altitude region above 27 km. Hence the stratosphere is divided into two separate regions [*Bischof et al.*, 1985]: the transition layer, which starts immediately after the tropopause and extends up to about 27 km, and the undisturbed upper stratosphere, which is located above the transition layer. At the ceiling altitude of this flight (~37 km) its concentration is observed to be 2.33±0.05 (1σ) pptv. The decrease in abundance with altitude in the various altitude regions is dependent on the coupled chemical and dynamical processes and has different atmospheric implications.

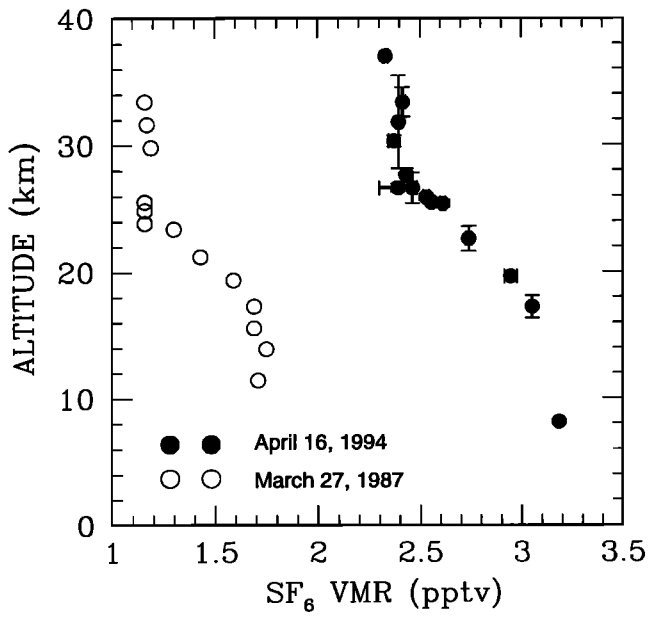

Figure 1. Comparison of vertical profiles of SF_6 measured over Hyderabad during April 16, 1994 (solid circles), and March 27, 1987 (open circles). Horizontal error bars are showing 1σ spread of the SF_6 VMRs and the vertical bars are indicating the altitude range of air sampling.

Vertical profiles of this gas are very limited in the tropical region; the only other measurement available in the literature is that of *Harnisch et al.* [1996] obtained on March 27, 1987, during a collaborative experiment between PRL and Max-Planck-Institut für Aeronomie, Germany. A comparison (see Figure 1) with the present measurement also shows a large increase in its concentration from 1987 to the present at all the altitudes; however, the main features are fairly similar.

Model Calculation

Loss mechanisms of SF_6 in the atmosphere are not yet understood clearly. There have been very few efforts to explain its vertical profiles, which were observed mainly in the lower stratosphere. *Ko et al.* [1993] found that the model vertical profile computed assuming a loss rate similar to that of CFC-11 in the stratosphere appears to follow the same trend as the SF_6 mean vertical profile retrieved from the ATMOS/ATLAS 1 occultation spectra observed during March-April 1992 in the latitude range 27.6^{0}S to 54.2^{0}S [*Rinsland et al.*, 1993]. But comparisons of the simultaneously measured vertical distributions of CFC-11 and SF_6 on April 16, 1994, and March 27, 1987 (not shown here), do not seem to support their result.

We have used the NASA/GSFC two-dimensional (2D) photochemistry and transport model to simulate the distribution of sulphur hexafluoride. The GSFC 2D model is described by *Jackman et al.* [1996]. Its vertical range, equally spaced in log pressure, is from the ground to approximately 90 km (0.0024 mbar) with approximately a 2-km grid spacing. Latitudes range from 85^{0}S to 85^{0}N with a 10^0 grid spacing. The climatologically based transport consists of a residual circulation and diffusion computed by using a 17-year average (1979-1995) of temperature data from the National Centers for Environmental Prediction. The transport fields change daily but repeat yearly.

Vertical profiles of SF_6 have been computed using the tropospheric inventories proposed by *Maiss et al.* [1996]. In this calculation, three different loss rates are assumed: With no photochemical loss the model results are in fairly good agreement with the observed

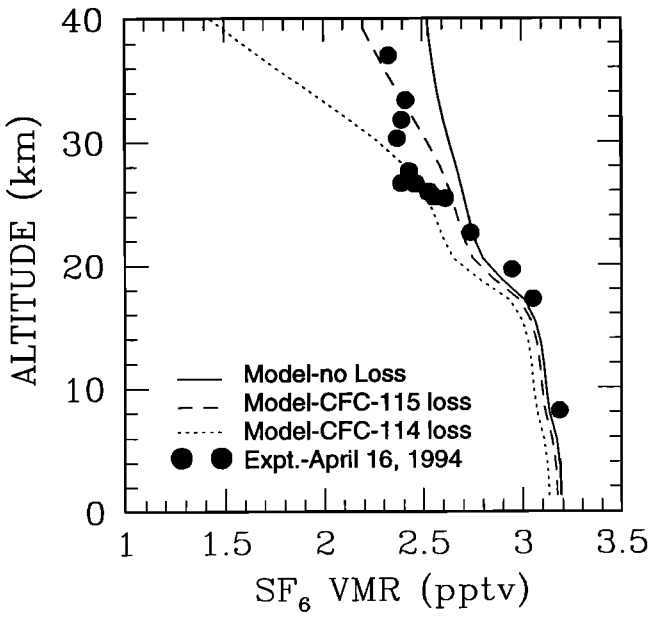

Figure 2. Balloon measurements obtained on April 16, 1994, and two-dimensional model results computed assuming various loss rates for SF_6 (see text for details).

abundances; however, because of the limitations of the 2D model, detailed structures observed in the measurements could not be explained. Loss rates identical to those of CFC-115 and CFC-114 have been used to compute SF_6 vertical distributions. The latter two derived profiles show much larger gradients, particularly above the transition layer. These results are depicted in Figure 2 along with the distribution on April 16, 1994. This comparison clearly suggests that the vertical profiles of sulphur hexafluoride follow the no loss type of trend in the vertical distribution and do not show any significant photochemical loss in the stratosphere.

Age of the Stratospheric Air

Because there is no significant chemical loss of SF_6 in the stratosphere, the decrease in volume mixing ratio (VMR) with altitude is attributed to the transport time of the air parcel from the troposphere to the various stratospheric altitudes. Time series measurements of SF_6 at the surface exhibit a quadratic increase in its abundances [*Maiss and Levin*, 1994; *Maiss et al.*, 1996]. This near-linear increasing trend in mixing ratio of an atmospheric constituent with no measurable loss in the stratosphere is appropriate to estimate the "age" of stratospheric air from its vertical profile [*Hall and Plumb*, 1994]. When we correlate the surface VMR of SF_6 as a function of time with stratospheric VMRs, the estimated age of the air varies from 4.1 to 4.6 years with an average value of 4.26±0.17 years (1σ) in the altitude region of about 27 to 37 km on April 16, 1994. These "age" values are comparable with the theoretical age spectrum, provided the sources of SF_6 are located near 43^0N [*Hall and Plumb*, 1994]. The time lags between stratospheric and tropospheric air observed by various authors are given in Table 1. A mean delay time between tropospheric and stratospheric air (altitude more than 22 km, 44^0N) was reported to be 5 years from the vertical distributions of CO_2 measured over midlatitude [*Bischof et al.*, 1985], a result supported by *Schmidt and Khedim* [1991], who found it to be 5.6 years. Recent observations of SF_6 over midlatitude and arctic polar region inferred an age of air above 19 km altitude to be 3.8 years and 5.7 years, respectively; however, the age of stratospheric air continues to increase above 25 km (8 to 9-year old air was found at 30 km) [*Harnisch et al.*, 1996]. This effect is probably due to the subsidence of high-altitude air inside the polar vortex. Inside the arctic polar lower stratosphere the age of air has been adopted to be 4 years in evaluating the ozone depletion potentials [*Pollock et al.*, 1992]. Below 17 and above 27 km the age of air does not change much with altitude. The regions below 17 and above 27 km are mixed much more rapidly than those in between.

Atmospheric Lifetime of Sulphur Hexafluoride

Nitrous oxide (N_2O) and CFC-12, which have longer photochemical lifetimes than the quasi-horizontal transport timescales, attain slope equilibrium and exhibit a linear relationship that can be related in turn to the ratio of their atmospheric lifetimes by the following equation [*Plumb and Ko*, 1992]:

Table 1. Age of Stratospheric Air Calculated From Long-Lived Atmospheric Trace Gases

Location	Period	Gas	Age, years	Reference
44^0N	1979-1984	CO_2	~5	1
44^0N and 52^0N	1976-1988	CO_2	5.6±1.1	4
44^0N and 68^0N	1988-1990	CO_2	2.3±0.3	4
62^0N-89^0N	1989	F-115	4.4±1.25	3
44^0N	1983 and 1993	SF_6	3.8	2
68^0N	1992 and 1995	SF_6	5.7	2
17.5^0N	1987	SF_6	4.7	2
17.5^0N	1994	SF_6	4.26±0.17	5

1, *Bischof et al.* [1985]; 2, *Harnisch et al.* [1996]; 3, *Pollock et al.* [1992]; 4, *Schmidt and Khedim* [1991]; 5, this work.

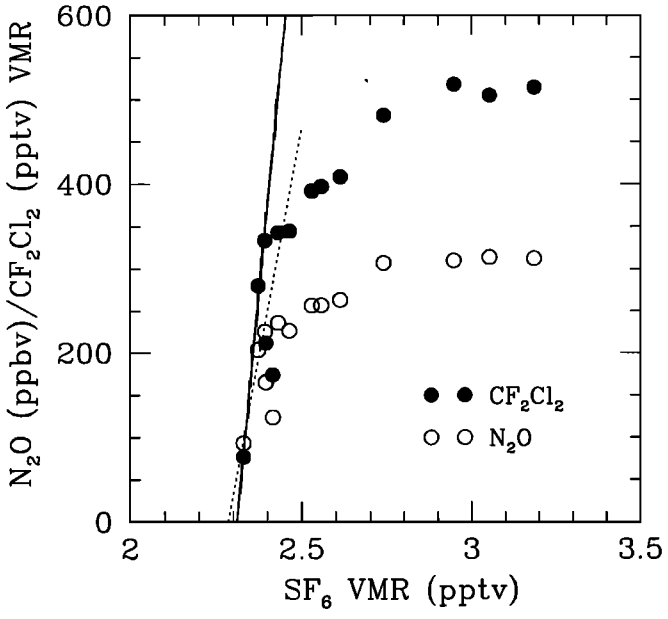

Figure 3. Middle stratospheric intercorrelations of sulphur hexafluoride with N_2O and CFC-12 (CF_2Cl_2). The straight lines can be expressed as (1) dashed line: [N_2O] (ppbv) = 2181.8 [SF_6] (pptv) - 4987 ppbv (R^2=0.97) and (2) solid line: [CFC-12] (pptv) = 4195.2 [SF_6] (pptv) - 9693 pptv (R^2=0.99) for SF_6 mixing ratio $\leq$ 2.395 pptv.

$$\frac{\tau_x}{\tau_y} = \frac{dy}{dx} \cdot \frac{\sigma_x}{\sigma_y} \qquad (1)$$

where the σs are representative of the tropospheric mixing ratios, dy/dx is the slope of the correlation curve, and the τs are atmospheric life times of the gases under study. Similar compact relationships of simultaneously measured N_2O and CFC-12 with SF_6 are investigated here (Figure 3). Vertical distribution profiles of N_2O and CFC-12 are taken from *Lal et al.* [1994, 1996]. Third-order quadratic fits are found to be in good agreement in the complete altitude range (not shown); however, above the transition layer, where the loss of SF_6 due to reactions with OH, $O(^1D)$ are proposed, simple linear fits are apparent. Using equation (1) and various probable interrelationships between SF_6 and N_2O and SF_6 and CFC-12 for $SF_6 \leq 2.5$ pptv, we find atmospheric lifetimes of SF_6 of 1937±432 (1σ) years. The best fits for SF_6 VMR $\leq$ 2.395 pptv are only shown in Figure 3 (similar correlations of 1987 data have not been used for calculating lifetime, as we have observed a significant effect of dynamical perturbations in the N_2O and CFC-12 vertical profiles). Atmospheric lifetimes of N_2O and CFC-12 are taken to be 120 and 102 years, respectively, for these calculations [*World Meteorological Organization*, 1995]. Lifetimes calculated from the best fits shown Figure 3 are in good agreement with each other. However, this value is much shorter than the best estimate of *Ravishankara et al.* [1993], which is 3200 years. *Ko et al.* [1993] calculated an effective atmospheric lifetime of about 900 years with an extra loss term included due to the photodissociation of SF_6 caused by UV radiation ($\lambda \leq 240$ nm). To check for validity of equation (1) for the tropical region, assuming a lifetime of 102 years for CFC-12, we calculated an atmospheric lifetime of 119 years for N_2O, which matches very well with that used in this calculation.

Conclusions

We confirm that SF_6 has a very long atmospheric lifetime. Its very small atmospheric loss, which has been shown by using 2D model results, in contrast to the previous studies, and rapid increase in atmospheric burden combine to make sulphur hexafluoride extremely useful to study the tropospheric and stratospheric dynamical processes. The vertical distribution measured from Hyderabad shows a transition layer between the tropopause and 27 km height. Above the transition layer the age of the air is found to vary from 4.1 to 4.6 years. An atmospheric lifetime of about 1937 years has been calculated from stratospheric mixing ratio interrelationships of SF_6 with simultaneously observed vertical distributions of N_2O and CFC-12.

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