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Role of middle atmosphere coupling processes in ozone change

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The earth's middle atmosphere is a complex region where processes like radiative transfer, chemistry and dynamics are nonlinearly coupled. The relationship between ozone concentration and temperature at stratospheric level and the solar UV irradiance and the total ozone column density are shown as examples of coupling processes. One of the recent findings on the role of stratospheric aerosols in depleting ozone concentration through heterogeneous chemistry is highlighted.

THE altitude region extending between 10 and 100 km of the Earth's atmosphere is generally defined as the 'middle atmosphere'. It can be said that the middle atmosphere couples the upper ionospheric region with the meteorologically significant lower part of the atmosphere, as it is influenced from both above and below. It is a complex region where processes like radiative transfer, chemistry and dynamics are nonlinearly coupled. Systematic observations of this region have begun only in the last ten to twenty years using rocket, balloon and satellite-borne sensors and also using more versatile ground-based techniques such as lidar. Atmospheric ozone is a very important constituent of the middle atmosphere whose global distribution is determined by several chemical as well as physical processes. Detailed experimental and theoretical studies of the behaviour and transport of ozone started way back in the 1940s, and attempts were made to bring out the dependence of ozone distribution on meteorological parameters[1-3]. Extensive literature is available on ozone studies conducted since then (WMO Report[4] and references cited therein). However, over the past few years there has been a greater concern about the anthropogenic influences which are found to play a major role in depleting the ozone abundance. The major consequence of ozone depletion is an increase in the biologically active ultraviolet (UVB) radiation received at the surface apart from its impact on climate through radiative forcing. In this work some of the recently found middle atmospheric processes which influence the ozone chemistry are presented. Particularly the recent finding on the significance of stratospheric aerosols in depleting the ozone concentration through heterogeneous chemistry is highlighted.

Examples of coupling processes

The classic example of a coupling process going on in the earth's middle atmosphere is between two regions, the troposphere and the stratosphere, through meridional circulation. The rising motion of air in the tropics and the descending motion at the mid-latitude regions, referred to as the 'Hadley cell' is used[5] to explain the observed latitudinal increase in the column density of ozone although the ozone production is maximum at the tropical upper stratosphere. Thus the spatial and temporal distributions of ozone depend not only on the chemical reactions which produce and destruct the ozone molecules but also on dynamics which can transport ozone as well as other minor constituents involved in the ozone chemistry.

The temperature field which determines the rates of many chemical reactions is also found to play a role in
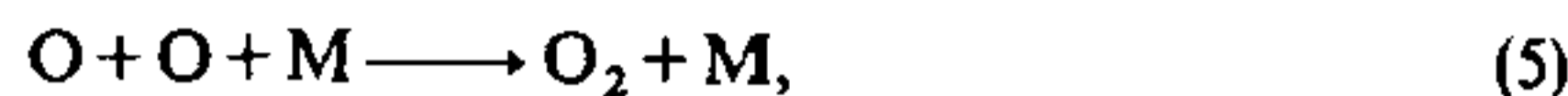
the ozone distribution. It is known that the absorption of solar ultraviolet radiation by the ozone molecules is the major source of heat in the stratosphere and mesosphere. Hence at these altitudes for any change in ozone concentration there is a corresponding change in temperature. Dickinson[6] has shown that for a 10% reduction in ozone, at 50 km for example, the temperature will fall by about 5°K in response. However this is an approximate estimate only as it ignores other feedback mechanisms such as the variations induced in the cooling rate due to changes in the amount of infrared emission at 9.6 μm by the ozone molecules. Also a change in temperature will modify the rates of several chemical reactions. For example the rates of reactions (2) and (3) given in the following section depend on temperature[7]. While reaction (2) which produces ozone molecules is inversely proportional to temperature, the rate of reaction (3) which destruct ozone depend directly on temperature. The net effect is that a reduction in temperature will result in an increase in ozone concentration. In real atmosphere both effects occur simultaneously and a feedback mechanism is established between these two processes[8]. A more realistic analysis must also include reactions involving other species such as hydrogen, chlorine and nitrogen. An observational evidence of ozone-temperature coupling is illustrated by Krueger et al.[9] using satellite data, in which the amount of ozone and temperature anticorrelate at an altitude of around 45 km and correlate positively in the lower stratosphere.

Another important coupling is between the incoming solar radiation intensity and the ozone concentration. The natural variations in the solar energy input to the earth's atmosphere such as the 27-day period oscillation or the 11-year solar cycle are expected to induce positive response in the ozone production rate. While most of the earlier works[10] are biased to individual stations and other meteorological parameters, recently, Keating et al.[11] analysed 12 years (from 1978 to 1990) of TOMS (Toral Ozone Mapping Spectrometer onboard Nimbus-7) Satellite data on total column density of ozone and the 10.7 cm solar flux data for the 40°S to 40°N latitude bin where the ozone production is the maximum and established a linear relation between the two.

In order to appreciate the recently found role of stratospheric aerosols in depleting the ozone concentration, a brief review of our understanding of ozone chemistry is in order.

Ozone chemistry

Using a steady state reaction scheme Chapman[12] in 1930 had proposed a set of five reactions:

$$O_2 + h\nu \longrightarrow O + O, \tag{1}$$

$$O + O_2 + M \longrightarrow O_3 + M, \tag{2}$$

$$O_3 + O \longrightarrow 2O_2, \tag{3}$$

$$O_3 + h\nu \longrightarrow O + O_2, \tag{4}$$

$$O + O + M \longrightarrow O_2 + M, \tag{5}$$

to predict the altitude distribution of ozone in a pure oxygen only atmosphere. It should be noted that the conversion between O and O_3 (reactions (2) and (4)) is so rapid that the photolysis of ozone (reaction (4)) is not an effective ozone loss mechanism. The measured stratospheric ozone concentrations are however far less than that estimated by Chapman's equations and the observed vertical distribution of ozone concentrations are also different which necessitate the inclusion of other ozone-depleting reactions to account for the additional loss processes of ozone.

The role of hydrogen compounds particularly the highly reactive OH radical in ozone chemistry was first examined by Bates and Nicolet[13]. The important chemical reaction involving OH is:

$$O_3 + OH \longrightarrow HO_2 + O_2, \tag{6}$$

followed by

$$HO_2 + O \longrightarrow OH + O_2, \tag{7}$$
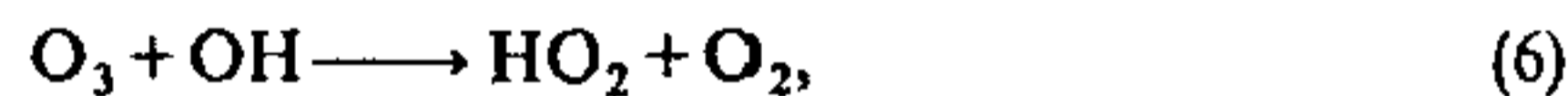
to give a net result of

$$O_3 + O \longrightarrow 2O_2. \tag{8}$$

The OH radical arises largely from the reaction of atomic oxygen with stratospheric water vapour (H_2O) where HO_2 stands for hydroperoxyl radical. The above chemical scheme is said to be catalytic because one OH molecule has the possibility of destroying many O_3 molecules.

The next important catalytic reactions involving NO_x molecules are brought out by Crutzen[14] and Johnston[15]:

$$O_3 + NO \longrightarrow NO_2 + O_2, \tag{9}$$

$$NO_2 + O \longrightarrow NO + O_2, \tag{10}$$
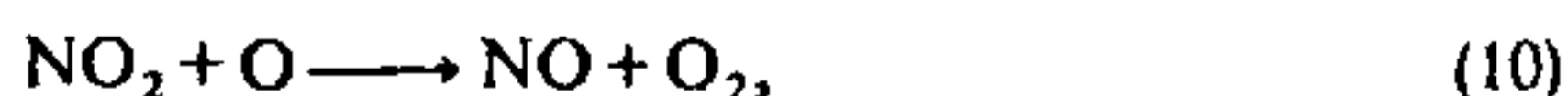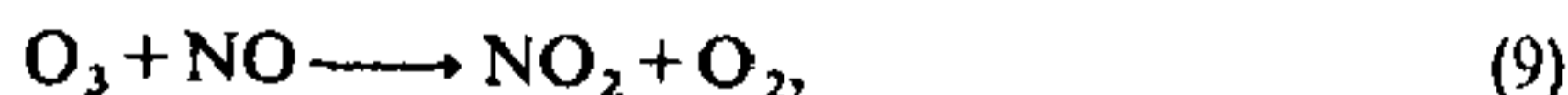
to give a net result similar to reaction (8). Nitric oxide (NO) is produced at the stratospheric levels from the reaction of nitrous oxide (N_2O) with atomic oxygen where N_2O is a natural biospheric emission. It should be noted that the NO_x molecules present at large quantities in a polluted environment can help to produce ozone molecules at lower tropospheric altitudes.

The resultant tropospheric ozone increase and their contribution to 'greenhouse warming' are beyond the scope of the present work.

Molina and Rowland[16] pointed out the significance of chlorine atoms in catalytically destroying ozone molecules at stratospheric altitudes:

$$Cl + O_3 \longrightarrow ClO + O_2, \tag{11}$$

$$ClO + O \longrightarrow Cl + O_2. \tag{12}$$

Chlorine atoms are produced in the stratosphere mainly by the ultraviolet photolyses of anthropogenic chloroflurocarbons (CFCs) which are however inert in the troposphere.

It should be noted that in all the above three reaction schemes the reactants (OH, NO and Cl) which dissociate the ozone molecules are produced back in the subsequent reaction to restart the catalytic destruction cycle. The various reaction cycles involving HO_x, NO_x, ClO_x, and BrO_x are so coupled that the overall homogeneous (gasphase) chemistry at stratospheric altitudes are quite complicated.

Ozone distribution and trends

Figure 1 shows the mean vertical distribution of ozone concentration over Thumba[17] (8.5°N) in southern India. Results of 19 rocket measurements made at Thumba are used to obtain a mean profile in the altitude region of 20 to 60 km and the results from several balloon measurements conducted by the India Meteorological Department are used at the lower altitude region. The horizontal bars represent two standard deviations of the mean value. The maximum ozone concentration over tropical site is found at around 27 km. The important difference between the ozone profiles over any tropical region and a higher latitude region is that the altitude at which the maximum ozone concentration occurs decreases with increasing latitude. The ozone concentration values are also found to be higher at higher latitude regions. This observed latitudinal difference in the ozone concentration is attributed to atmospheric dynamics as described earlier.

In one of their recent publications Subbaraya et al.[18] have compared the mean ozone mixing ratio (ozone density to air density ratio) profiles obtained over Thumba during the three major ozone measurement campaigns conducted in March 1983, December 1987 and March 1990. Figure 2 shows the result of the comparison. While there is no appreciable change in the ozone values obtained in 1983 and 1987, the mean values obtained during 1990 are considerably lower in the altitude region between 30 and 40 km. As all the three profiles are averages of more than about fifteen individual rocket experiments conducted in a span of about a month any short-term variability is smoothed out in the averaging process. While the observed decrease can be attributed to long-term natural variations in the solar energy input, such as the 11-year solar cycle, and quasi-biennial oscillation (QBO) the catalytic destruction of ozone at stratospheric altitudes due to the increasing abundances of man-made CFCs cannot be ruled out.

After removing all possible natural variations analysis of the TOMS data for the last ten years revealed[19] a negative trend in the total column density of ozone at a rate of -0.2 to -3.0% per year at all mid- and high-
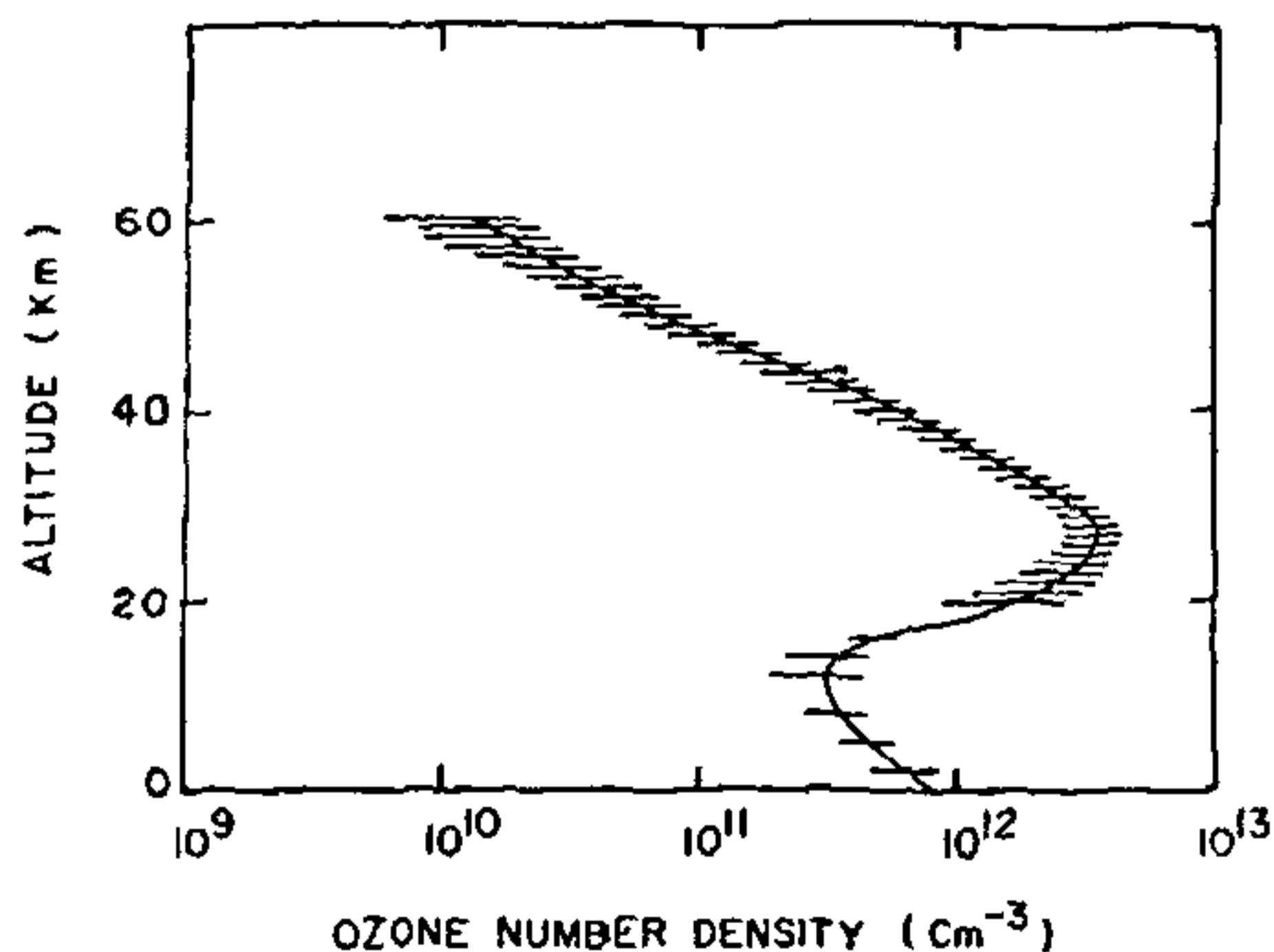

Figure 1. Mean values of ozone concentration obtained over Thumba (8.5°N) from rocket and balloon measurements. Horizontal bars represent two standard deviations of the mean value.
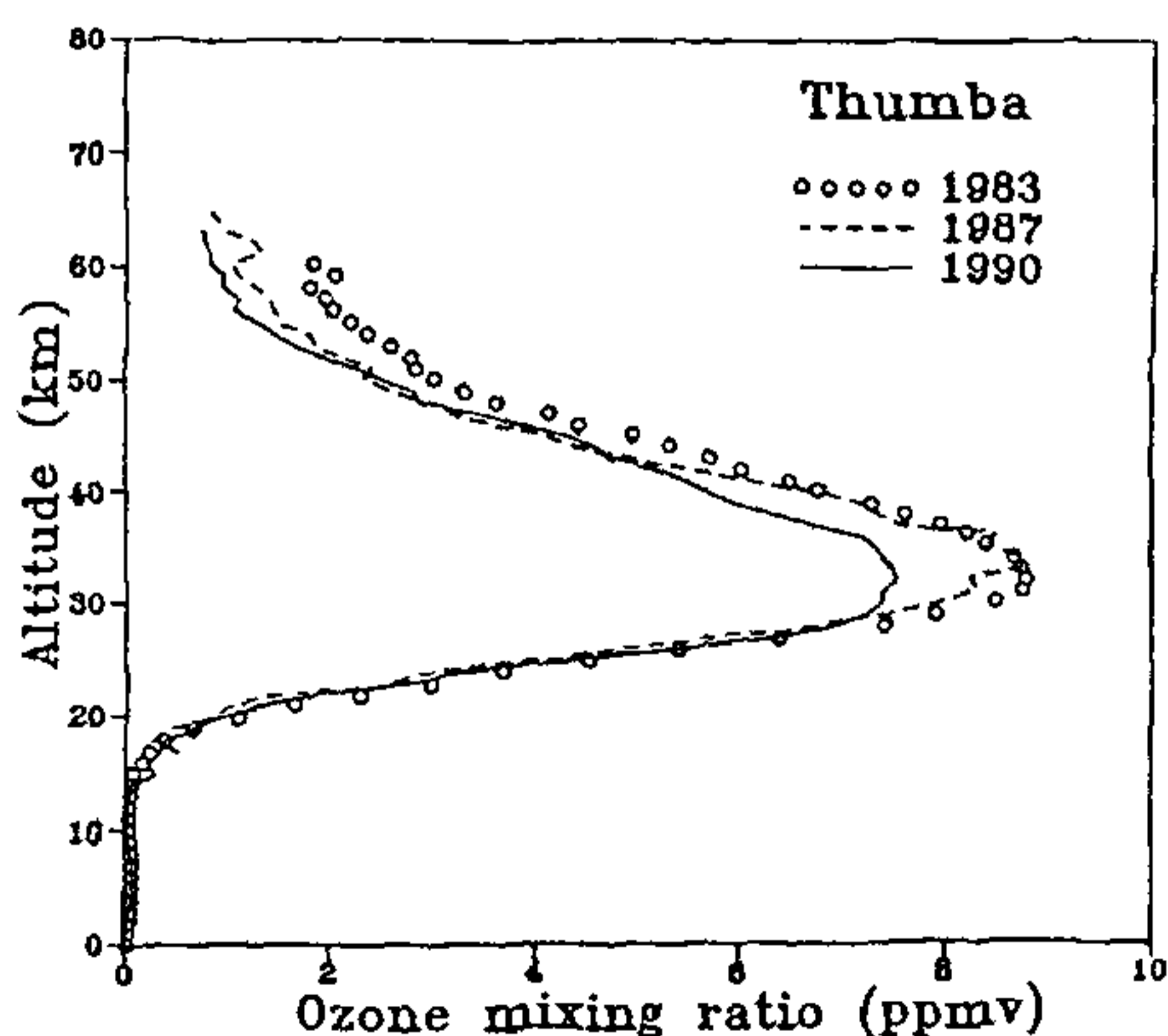

Figure 2. Comparison of the mean ozone mixing ratio profiles obtained during the three major rocket ozone measurement campaigns conducted at Thumba in 1983, 1987 and 1990.

latitude regions (Figure 3). The absence of any trend in the equatorial region is partly attributed to the increase in ozone concentration at tropospheric altitudes which compensate the observed negative trend in the stratosphere. The major anthropogenic source gases which destroy stratospheric ozone are CFC-11 ($CHCl_3$, trichloromethane) and CFC-12 (CF_2Cl_2, dichlorodifluoromethane. The 1989 global mean concentrations of CFC-11 and CFC-12 are found[20] to be 268 and 452 pptv respectively, increasing at a rate of 10.1 ± 0.1 and 16.9 ± 0.2 pptv per year.

The major consequence of ozone depletion is an increase in solar ultraviolet irradiance. The radiation amplification factor (RAF) defined as the ratio of the net change in UV irradiance to the net ozone change is found[21] to be 1.25 ± 0.20 implying that a 10% reduction in ozone density will cause a 11 to 15% increase in the biologically active ultraviolet (UV B) dosage at the Earth's surface.

Stratospheric aerosols and heterogeneous chemistry

Stratospheric aerosols are mainly H_2SO_4 (sulphuric acid) droplets and sulphate particles formed from precursor gases such as sulphur dioxide (SO_2) and carbonyl sulphide (OCS) transported into the stratosphere from the troposphere or directly injected there during major volcanic eruptions. Figure 4 depicts a simplified scheme showing the physical and chemical processes involved in the formation of stratospheric aerosols from gases. The gas to particle conversion mechanism consists of a series of chemical transforma-

Figure 4. Schematic of the stratospheric aerosol formation from precursor gases.

tions followed by condensation mechanism. Evolution of the stratospheric aerosol layer involves a variety of physicochemical interactions such as vapour nucleation, condensation and evaporation, coagulation, gravitational sedimentation and dynamical transport. The vertical distribution of aerosol concentrations show large spatial and temporal variations. The stratospheric aerosols are generally in the size range of 0.05 to 0.5 μ and have a relatively longer residence time of 2 to 3 years compared to tropospheric aerosols.

The results of aerosol measurements made at Thumba and Hyderabad using rocket and balloon-borne optical measurements[22,23] are shown in Figures 5 a,b. Aerosol concentration is in general found to vary between a few hundred particles per cubic centimetre at 5 km and a few particles at 30 km region. The size distribution of aerosol particles at higher altitudes is in
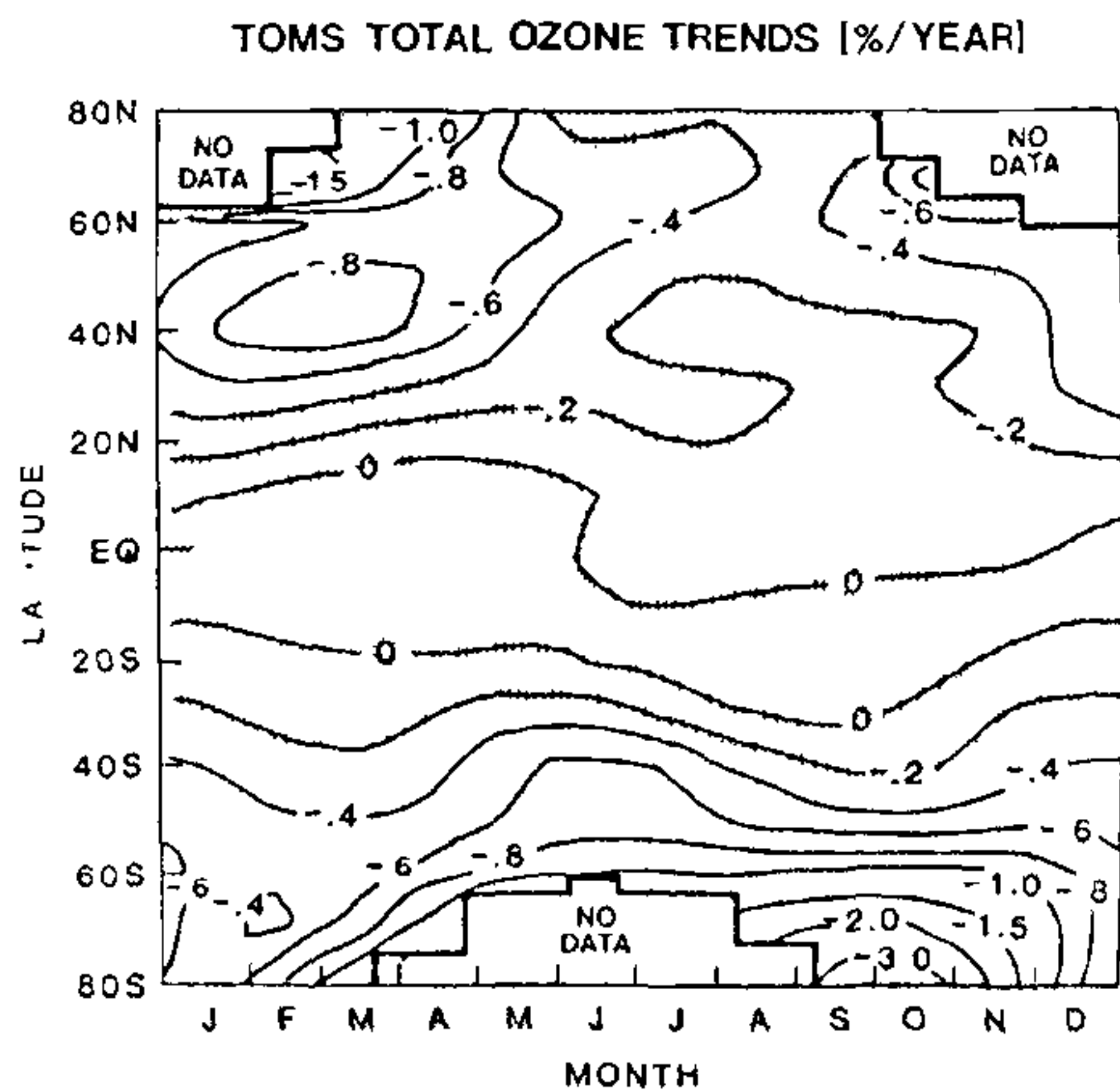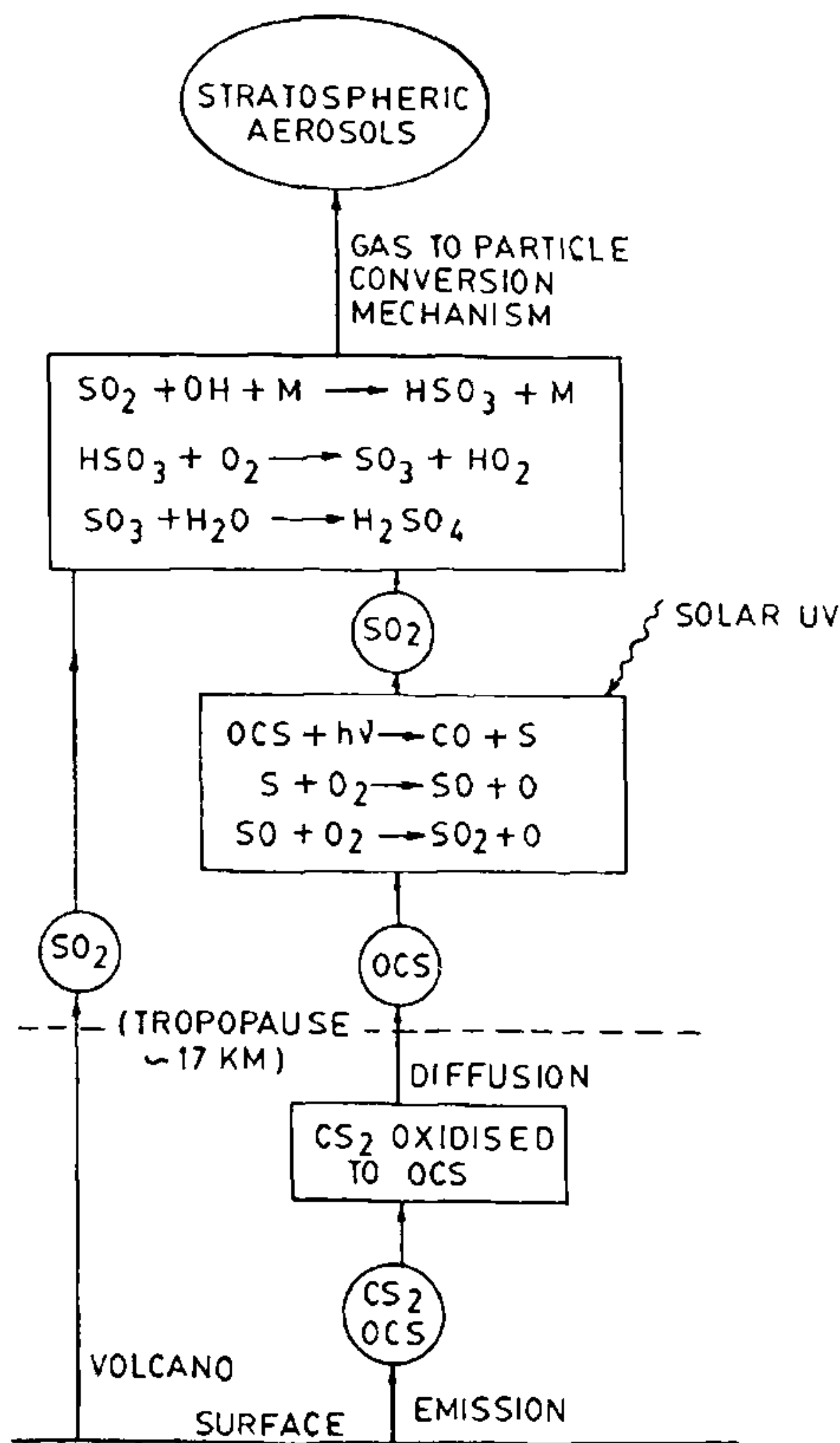
TOMS TOTAL OZONE TRENDS [%/YEAR]

Figure 3. Global ozone trend in percentage per year, derived from the TOMS (Total Ozone Mapping Spectrometer, onboard Nimbus-7 satellite) ozone data for the period 1979 1990.
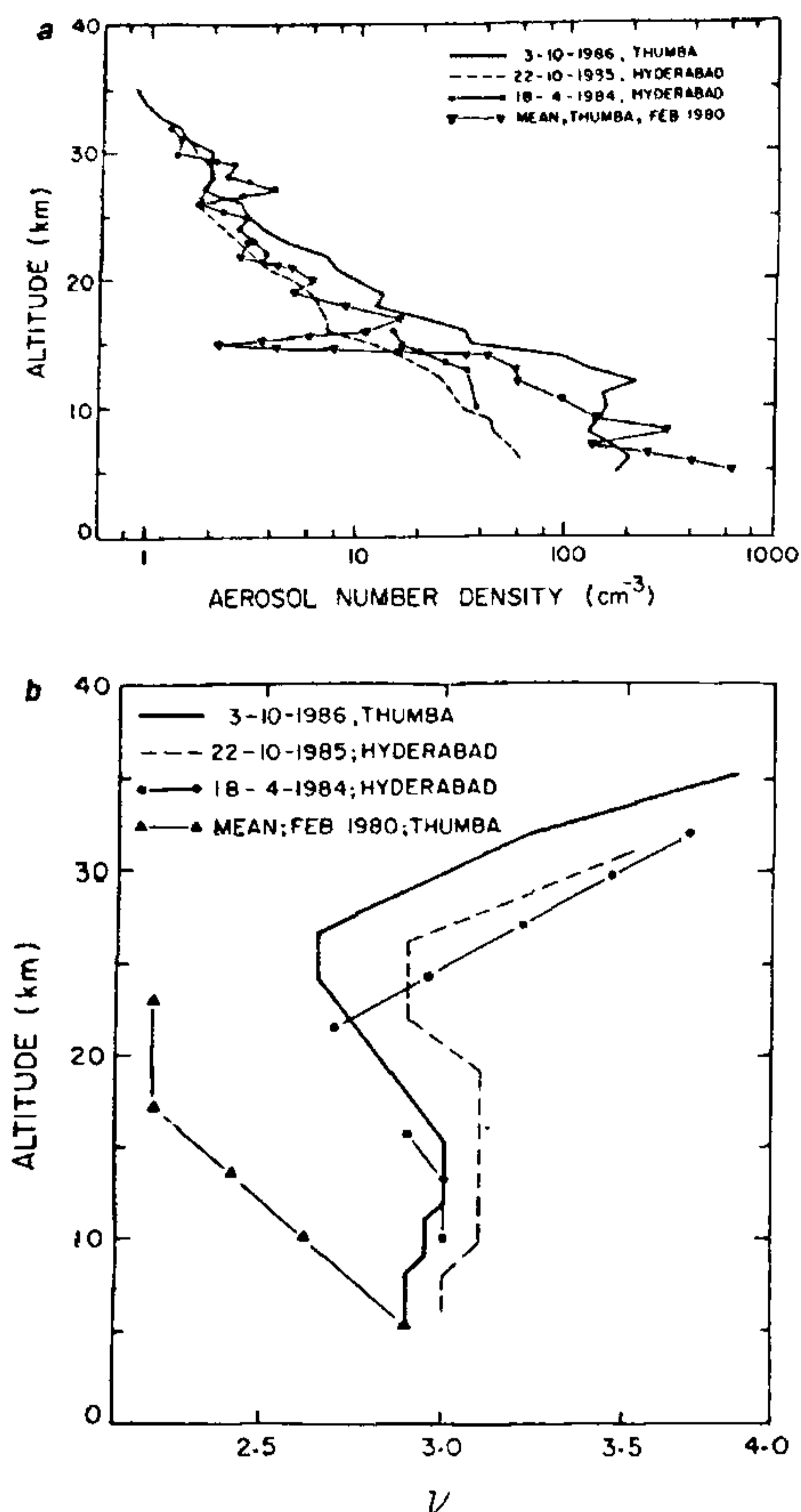

Figure 5. Vertical profiles of (a) aerosol concentration and (b) size distribution function obtained over Thumba and Hyderabad from rocket and balloon-borne measurements respectively[22,23].

general found to be a power law distribution and is expressed by a size parameter v, the slope of the power law curve. Low v values imply a relatively larger number of bigger particles in a given ensemble. Figure 5b shows the altitude profiles of v derived from the measurements. The stratospheric aerosol layer can be seen in the 20 to 25 km region as a decrease in the v value. Low v values obtained during the 1980 rocket measurements over Thumba were found to be due to the influence of Sierra Negra volcano (0.8° S, 91.2° W) erupted on November 13, 1979, three months prior to the measurements. In the case of the 1984 measurement, the influence is due to the El Chichon eruption in
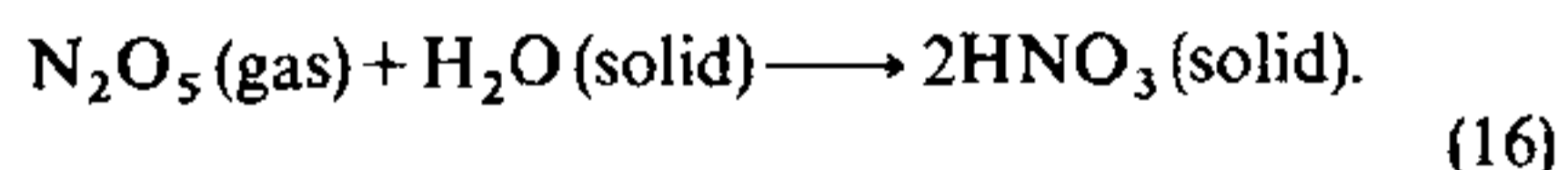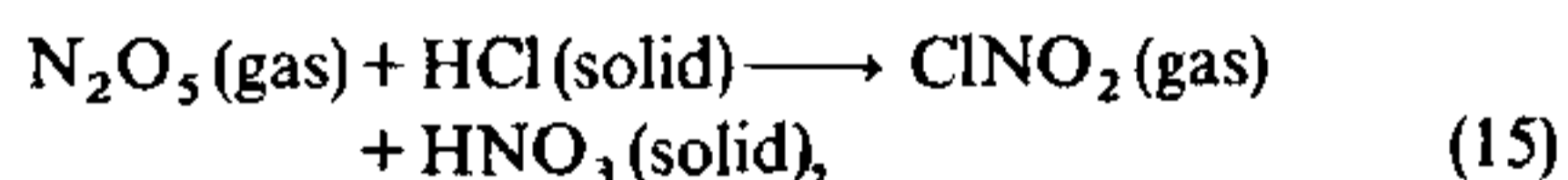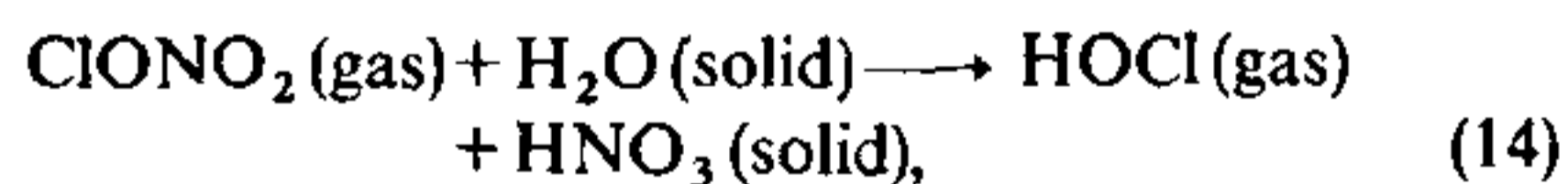
Mexico in April 1982, the effect of which had not subsided even after two years.

In recent times there has been great concern about the role of stratospheric aerosols in depleting ozone molecules. Importance of aerosols in accelerating certain ozone-depleting chemical reactions has been realized in order to explain the observed[24] spring time loss of ozone, called the 'ozone hole' over the south pole region. For example Figure 6 shows the comparison of the October monthly mean TOMS data over the Antarctica region for the last five years. The 1991 map shows a deep minimum with the lowest total column of ozone ever observed over Antarctic which is less than 150 DU (one Dobson Unit equals 2.687×10^{16} molecules per cm^2). The corresponding ozone values over the same region and season were well above 300 DU before 1970. Satellite and balloon measurements have revealed that over Antarctic the ozone depletion starts during September in the altitude region of 14 to 22 km and by October the ozone concentration is found to fall by as high as 95%. Laboratory measurements and extensive field measurements have also proved that this severe ozone damage is primarily due to chlorine and bromine atoms liberated at these altitudes. Also at midlatitude regions the observed negative trend in the ozone amount could be explained[25] better after the inclusion of heterogeneous reactions involving aerosols and gases in the model calculations than using only the gasphase chemistry.

Following the discovery of Antarctic ozone hole Soloman et al.[26] have suggested the following heterogeneous reaction:

$$ClONO_2(gas) + HCl(solid) \longrightarrow Cl_2(gas) + HNO_3(solid) \tag{13}$$
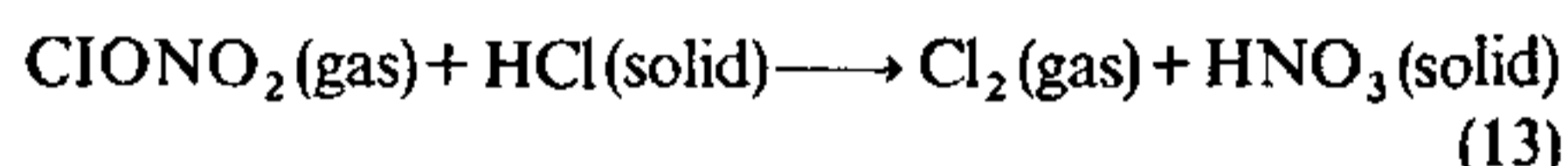
in which inactive chlorine from the reservoir species HCl is liberated as an active chlorine molecule which can rapidly be dissociated into chlorine atoms in sunlight to initiate the catalytic destruction of ozone. Examples of other heterogeneous reactions are:

$$ClONO_2(gas) + H_2O(solid) \longrightarrow HOCl(gas) + HNO_3(solid), \tag{14}$$

$$N_2O_5(gas) + HCl(solid) \longrightarrow ClNO_2(gas) + HNO_3(solid), \tag{15}$$

$$N_2O_5(gas) + H_2O(solid) \longrightarrow 2HNO_3(solid). \tag{16}$$

The terms 'solid' and 'gas' represent solid phase or adsorbed into a solid surface and gas phase respectively. The solid phase HNO_3 (nitric acid trihydrate or NAT) and water ice are generally referred to as polar stratospheric clouds (PSC) types I and II respectively. Type I PSC particles form at temperature around
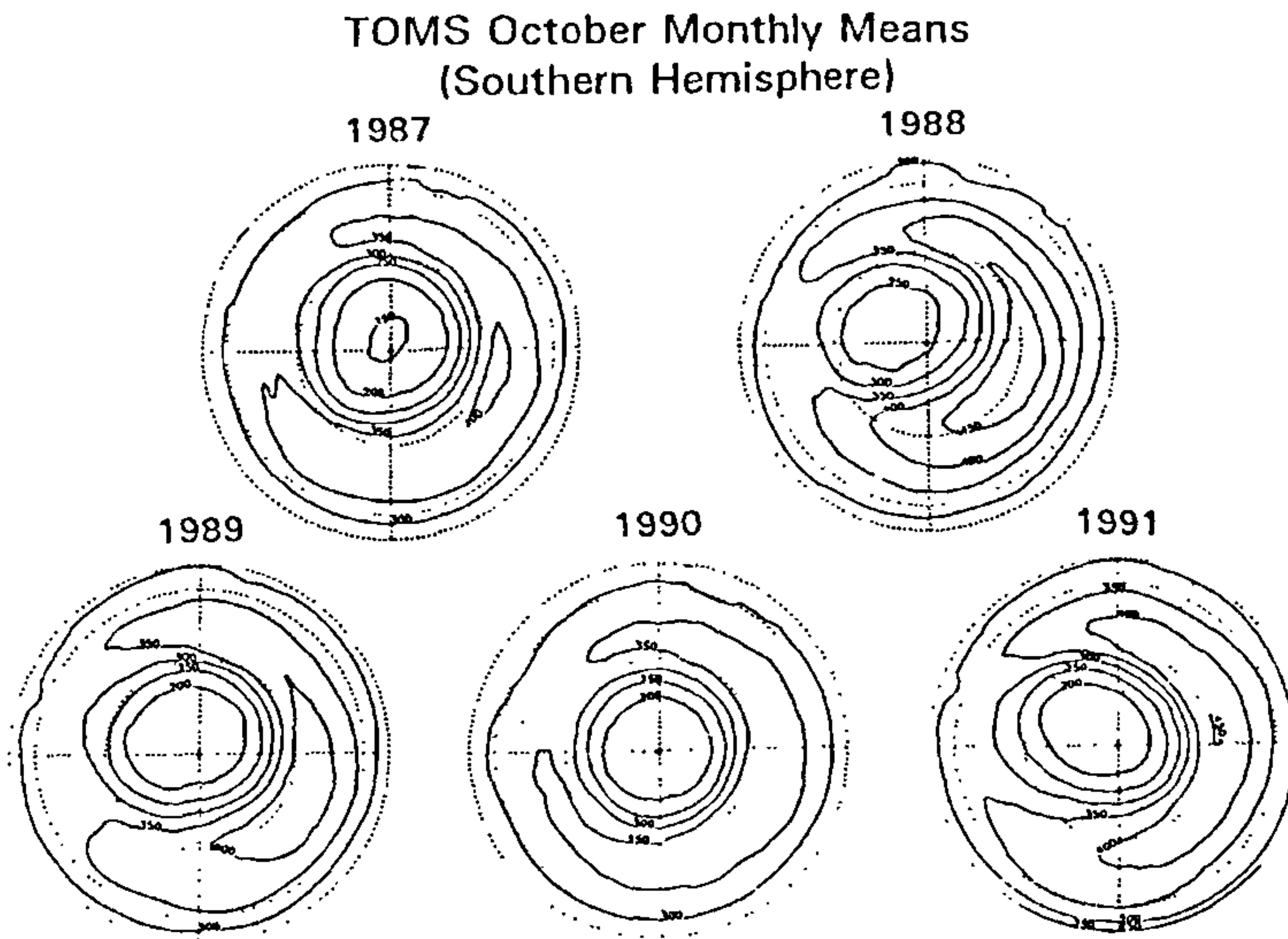
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TOMS October Monthly Means
(Southern Hemisphere)

1987   1988

1989   1990   1991

Figure 6. Polar orthographic projection of TOMS data on the October mean total ozone values expressed in Dobson units South pole is at the centre. The equator, 30° S and 60° S, is shown by dotted circles[29].

195° K, about 4 to 6° K above the ice point at which type II PSCs are formed. The heterogeneous reactions are most prevalent in the 10 to 25 km altitude region where the ambient low temperatures are conducive to PSC formation[27].

Stratospheric aerosols can act as catalysts by providing necessary surface area for various heterogeneous chemical reactions. In the last 10 years there have been two major volcanic eruptions, namely El Chichon in Mexico which erupted in April 1982 and more recently the Mt. Pinatubo eruptions at Philippines in June 1991. Mt. Pinatubo eruption is most likely to be the greatest of this century. Satellite data show[28] that the stratospheric aerosol extinction coefficients have increased by about 1 to 2 orders of magnitude after this eruption. Figure 7 shows the result of the Nd:YAG Lidar measurement made at PRL, Ahmedabad in May 1992. The number of photons back-scattered from various altitude levels is measured with an altitude resolution of 96 metre. An order-of-magnitude increase is seen in the back-scattered photon from the altitude region of about 19 to 26 km showing the presence of the Pinatubo volcanic aerosol layer over Ahmedabad, about an year after the eruption. This perturbation is expected to last over the entire globe for the next four to five years. As these aerosols serve as nuclei for the PSC formation, it is reasonable to estimate that the effective aerosol surface area available for heterogeneous

chemical processing might have increased comparable to the observed increase in the aerosol amount, which can further accelerate the ozone depletion mechanisms.
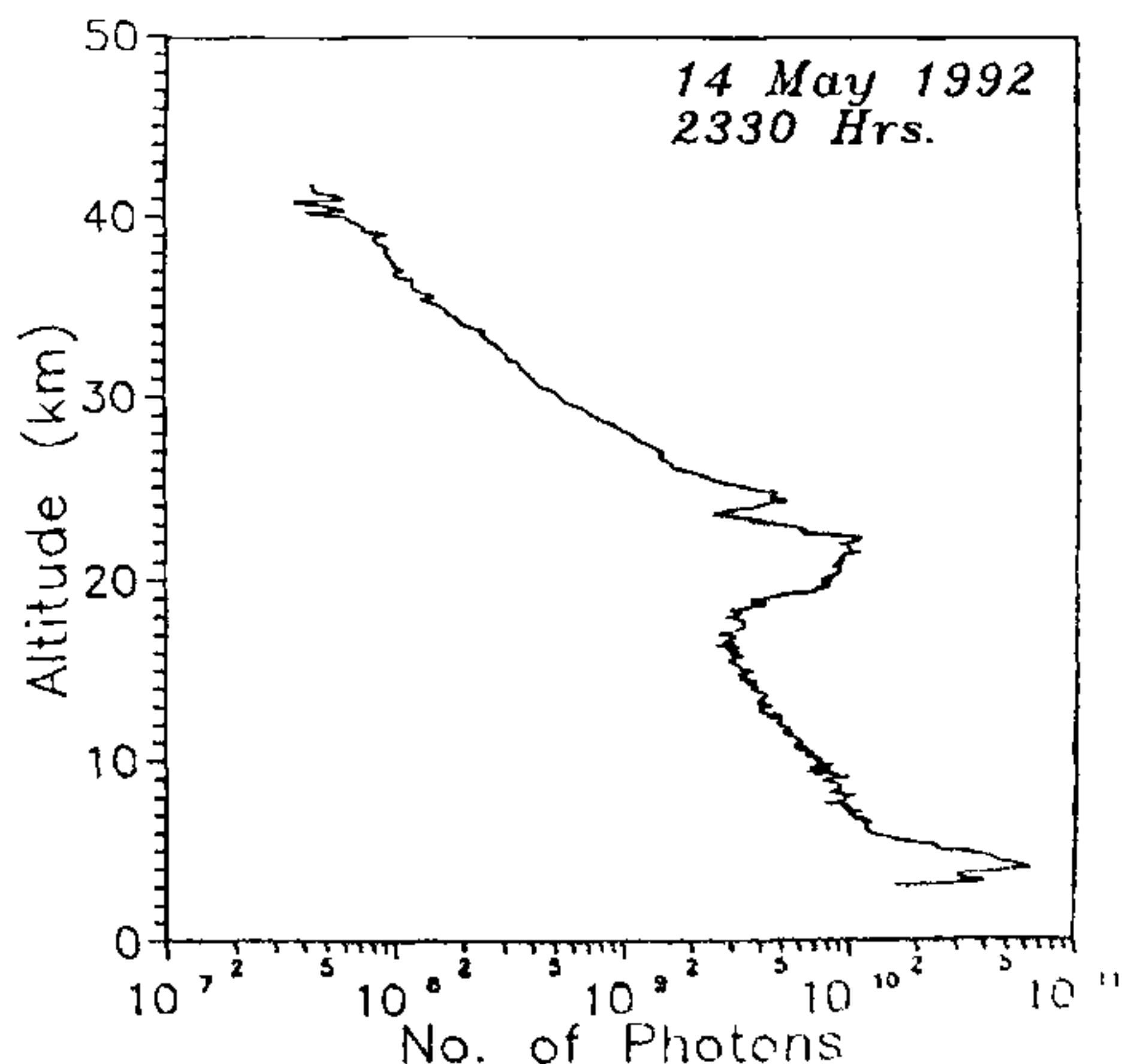
Figure 7. Result of Nd YAG Lidar measurement made at PRL, Ahmedabad. The profile shows the backscattered radiation intensity A double humped stratospheric aerosol layer is seen in the 19 to 26 km region, formed due to the Mt. Pinatubo volcanic eruption at Philippines in June 1991.

Summary

Satellite and other rocket and balloon measurements have revealed a negative trend in the total ozone concentration worldwide. The observed trend is higher over the mid- and high-latitude regions and is in the range between −0.2% and −3.0% per year. No appreciable trend has been found in the total ozone column density so far over the tropical regions. In spite of the voluminous data on the global distribution of ozone presently being collected using various satellite-borne sensors and the enormous amount of modelling effort, our understanding of the ozone depletion problem is still far from adequate. It is mainly because of the complex nature of the various physico-chemical processes going on in our earth's atmosphere. Several new chemical schemes have been proposed during the last two decades in order to explain the observed spatial and temporal variations of ozone concentrations. The recently found role of aerosols in depleting the ozone concentrations through heterogeneous chemistry has added another dimension to the ozone depletion problem.

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