Retrieval of stratospheric O₃ and NO₂ vertical profiles using zenith scattered light observations

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Daily zenith scattered light intensity observations were carried out in the morning twilight hours using home-made UV-visible spectrometer over the tropical station Pune (18°31', 73°51') for the years 2000–2003. These observations are obtained in the spectral range 462–498 nm for the solar zenith angles (SZAs) varying from 87° to 91.5°. An algorithm has been developed to retrieve vertical profiles of ozone (O₃) and nitrogen dioxide (NO₂) from ground-based measurements using the Chahine iteration method. This retrieval method has been checked using measured and recalculated slant column densities (SCDs) and they are found to be well matching. O₃ and NO₂ vertical profiles have been retrieved using a set of their air mass factors (AMFs) and SCDs measured over a range of 87–91.5° SZA during the morning. The vertical profiles obtained by this method are compared with Umkehr profiles and ozonesondes and they are found to be in good agreement. The bulk of the column density is found near layer 20–25 km. Daily total column densities (TCDs) of O₃ and NO₂ along with their stratospheric and tropospheric counterparts are derived using their vertical profiles for the period 2000–2003. The total column, stratospheric column and tropospheric column amounts of both trace gases are found to be maximum in summer and minimum in the winter season. Increasing trend is found in column density of NO₂ in stratospheric, tropospheric and surface layers, but no trend is observed in O₃ columns for above layers during the period 2000–2003.

1. Introduction

Changes in the concentration of the ozone (O₃) in the atmosphere by natural and human activities is a widely discussed subject. The distribution and trends of ozone in the atmosphere affect the climate system in several ways. Ozone in the stratosphere strongly absorbs solar ultraviolet (UV) radiation. A reduction in stratospheric ozone level, therefore, results in increased UV radiation levels in the troposphere and at the Earth's surface (WMO 1992). In the Earth's atmosphere, nitrogen dioxide (NO₂) exists as a trace gas with a large diurnal, seasonal, and latitudinal variation (Kreher *et al* 1995; Senne *et al* 1996). NO₂ plays an important role in ozone photochemistry, which is strongly dependent on the altitude. Below 25 km, NO₂ inhibits ozone destruction by converting active

chlorine and hydrogen species to inactive forms. On the other hand, NO₂ acts as a catalyst that accounts for removing almost half of the ozone by gas-phase reactions between 25 and 40 km layer. The combination of destruction cycle involving odd chlorine and bromine, odd oxygen, and odd hydrogen determines the photochemical balance of stratospheric ozone. Therefore, to understand stratospheric ozone loss, it is quite essential to know the vertical distribution of O₃ and NO₂.

Ground-based measurements include the Umkehr technique for measuring the profile of ozone concentration with the Dobson spectrophotometer at twilight (Gotz *et al* 1934). The Umkehr technique provides ~5 km vertical resolution for altitudes between 25 and 40 km along with low-resolution estimates above and below these altitudes. Ground based UV-visible spectrometer

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may give the vertical profiles of the atmospheric constituents with a lesser complicated process as compared to that used for the *in situ* measurements using balloon and aircraft-borne instruments (Mehra and Jadhav 1992; Londhe et al 1999). The ground based UV-visible spectrometer developed in the institute is used for the intensity measurements, which is described in detail by Meena (2005). The abundances of O₃ and NO₂ in the path of the sun rays, known as the slant columns, were determined from the absorption of sunlight scattered from the zenith sky during twilight using the ground based spectrometer (Solomon et al 1987; Bhonde et al 1992; Chakrabarty et al 1997; Meena et al 2003; Bhosale et al 2004). The slant column of absorbing species measured at twilight hours varies with solar zenith angle (SZA). Also it depends on the altitude of the absorber. Retrieval of the vertical distribution of trace gases like, O₃ and NO₂ from slant column density (SCD) measurements based on the weighted Chahine iterative method was first attempted by Brewer et al (1973) and later by Noxon (1975); McKenzie et al (1991), and Mehra and Jadhav (1992).

In the present study, we introduce an algorithm developed to derive vertical profiles of O₃ and NO₂ from slant column measurements. Daily routine observations of zenith sky intensity in the morning twilight hours at Pune (18°31', 73°51') were obtained during the period 2000–2003. These observations are utilized to derive the SCDs of O₃ and NO₂ that are used to retrieve their vertical profiles. Daily total column densities (TCDs) of O₃ and NO₂ are obtained by the integration of the vertical column densities (VCDs) of different layers. Also, the stratospheric and tropospheric columns of these gases have been derived. Comparison has been made between the vertical profiles obtained by Chahine iteration method and those obtained by Umkehr method and ozone sondes. Furthermore, TCDs obtained from vertical profiles and evaluated at 90° SZA on few days are compared. The day-to-day variability, interseasonal and interannual variability in the TCD of O₃ and NO₂ are discussed in the present study.

2. Air mass factors for vertical profile

In order to convert SCD to a VCD, it is necessary to divide the SCD by a factor which expresses the enhancement in optical paths through the atmosphere relative to the vertical optical path. This enhancement factor is referred to air mass factor (AMF) in the present study. The calculation of an accurate altitude dependent AMF is the basic requirement for the retrieval of the vertical profiles of the atmospheric trace constituents like O₃

and NO₂ (McKenzie et al 1991). The calculation procedure of altitude dependent AMFs has been discussed by Meena et al (2003). The weighted AMFs of the gas for a particular layer are calculated by assuming whole gas as accumulated in a single layer. In the algorithm, atmosphere is subdivided into 10 layers of thickness 5 km ranging from the ground to 50 km. The absorber is assumed to be uniformly distributed in every 5 km-thick layer. The AMFs are obtained by the Lambert–Beer's law:

$$I = I_o \exp(-\sigma \nu \delta) \quad (1)$$

where I and I_o are the attenuated and incident intensities received by the detector with and without the presence of the absorber respectively, σ is the cross section for extinction due to such processes as absorption and scattering by molecules, ν is the density of absorber or scatter, δ is the AMF.

The contribution to the intensity of scattered radiation at altitude z is given by the following equation:

$$I_{sc,z} = I_{d(z)} \sigma_R \nu_{air}(z) \Delta x \quad (2)$$

where $I_{sc,z}$ is the intensity of scattered radiation at layer z , $I_{d(z)}$ is the intensity of direct flux at altitude z , $\nu_{air}(z)$ is the air density at altitude z , σ_R is the cross section for Rayleigh scattering and Δx is the distance over which absorption takes place or optical path. If the intensity, absorption cross section, and absorber number density are known, then equation (1) may be inverted for the average enhancement in optical path length, or air mass factor

$$\delta = -\ln \frac{(I/I_o)}{\sigma \nu} \quad (3)$$

where the intensity I received by the detector in presence of absorber is calculated by a single scattering radiative transfer (RT) model. Absorption by O₃ and NO₂, together with Rayleigh scattering by air molecules and atmospheric number density (air density) are considered in the RT model used here. In the model, initial O₃ and NO₂ vertical profiles are assumed to follow Gaussian distribution with altitude.

Layerwise AMFs of O₃ and NO₂ used for retrieving the vertical profiles are respectively shown in figure 1(a and b). The AMFs are calculated for SZA between 87° and 91.5° at the interval of 0.5° SZA. Tropospheric AMFs calculated for O₃ and NO₂ are found to decrease with increasing SZAs. The calculated AMFs for O₃ and NO₂ located at 10–15 km appear to increase relative to those at 0–5 km due to the decrease in the Rayleigh scattering optical depth at this altitude range. Thus, at higher levels,

Figure 1. (a) Curves of O_3 and, (b) NO_2 air mass factors for each layer assumed 5 km-thick slabs.

the AMFs (enhancement factors) increase for the higher SZAs. The enhancement factors are maximum for the layer 20–25 km. For higher altitude layers, enhancement factors again decrease as compared to layer 20–25 km. These enhancement factors are used in the algorithm to retrieve vertical profiles of O_3 and NO_2 .

3. Algorithm to retrieve the vertical profiles of O_3 and NO_2

Increases in SCDs with SZAs are obvious because of scattering geometry: as the SZA increases,

the mean scattering altitude increases and rises into the absorber layer. Thus, the variations of SCDs with SZAs are dependent on the altitude of the peak abundance. Using the set of SCDs and enhancement factors, the vertical profiles of O_3 and NO_2 are retrieved by the Chahine iteration method.

For this study, the vertical column is subdivided into 10 assumed layers of thickness 5 km ranging from ground to 50 km. The sets of enhancement factors (AMFs) are used to generate the square matrix S_{ij} , in which i represents zenith angle, and j represents the number of layer. This matrix relates the change in apparent SCD of absorber in each

layer of the model. This can be expressed in a linear matrix model by the following equation:

$$F_i^m = S_{ij}C_j \quad (4)$$

where F_i^m is the corrected slant column amount at solar zenith angle i (m indicates 'modeled values'); S_{ij} is the air mass factor matrix at solar zenith angle i for an absorber in layer j ; C_j is the vertical column density (VCD) in layer j . Hence, each SCD is the weighted sum of contributions from all layers. The concentrations in each layer C_j , can be determined by solving the following matrix equation:

$$C_j = A_{ji}F_i^o, \quad (5)$$

here A_{ji} is the inverse of S_{ij} (if it is a square and nonsingular matrix) or least squares formulation, F_i^o is the observed SCD. In the process of obtaining solution using unconstrained linear method in the presence of noise in the measurement or the possible errors in the matrix inversion sometimes leads to negative concentrations in the particular atmospheric layers which seem to be quite unreasonable. Therefore, to avoid this, the Chahine iteration method is used for the retrieval of the vertical profiles.

The above matrix form of the equations is here called 'radiative transfer model' which is then solved to obtain the vertical profiles of atmospheric trace constituents using the above-mentioned weighted Chahine iteration method (Chahine 1977; Londhe et al 1999). In the Chahine iteration method, each model layer is assumed to be associated with a particular zenith angle, which is treated as a variable to obtain the different solutions. At the beginning, the process is started by assuming a first guess profile $C_j^{n=1}$ of the absorber for the first iteration. A new profile C_j^{n+1} , is then calculated by Chahine iteration method using the n th iteration of the solution profile (C_j^n) together with the linear model described above to calculate the expected modeled observations. The fitting errors between the observed and model predicted values (i.e., $F_i^o - F_i^m$) are computed and other iterations are made if these errors exceed a preset limit, where, F_i^o is the observed SCD and F_i^m is the model predicted value, and termed as recalculated SCD hereafter.

Chahine iteration method gives the $(n+1)$ th estimate of the concentration profile by the equation given below:

$$C_j^{n+1} = C_j^n \cdot \left(\frac{F_{k(j)}^o}{F_{k(j)}^m} \right), \quad (6)$$

where $k(j)$ represents the angle of layer j which has the largest enhancement factor. To limit the

number of iterations either maximum number of iterations should be specified in the program or the fitting error should approximately equal the estimated uncertainty in the observations. The sensitivity of this retrieval method to scattering model, SZA, initial guess profile, tropospheric pollution and the errors in the background absorption in the reference spectrum has been precisely described by McKenzie et al (1991). The next section gives the results and discussion on vertical profiles of O_3 and NO_2 retrieved using the above algorithm.

4. Results and discussion

The vertical profiles of the trace gases like O_3 and NO_2 , etc. are obtained from satellite, balloon and ground based instruments. The ozone profiles are obtained using various methods like lidar, ozonesondes and microwave radiometer. Ozonesondes are expected to provide reliable information of the vertical distribution of ozone in the troposphere and lower stratosphere below 30 km prior to the satellite measurements that started in 1979, but sondes are not always possible.

The Stratospheric Aerosol and Gas Experiment (SAGE), Solar Backscattered Ultraviolet (SBUV) and the Umkehr technique provide information of the vertical profile of ozone (e.g., Logan 1994; Hollandsworth et al 1995; Wang et al 1996; Harris et al 1997; Miller et al 1997). The satellite-borne remote sensing techniques with limb-viewing and nadir-viewing modes give a good vertical resolution of ozone, but only above the tropopause as the clouds obstruct measurements much below the tropopause level. Measurements of the profile in the troposphere with nadir viewers are difficult, as the instrument has to look through much larger stratospheric ozone content. Considerable differences are found between the ozone trends derived from ozonesondes and from the SAGE II instrument below about 20 km altitude (WMO/UNEP 1994). Above 20 km, considerably better agreement was found for the ozone trends measured by SBUV, SAGE and Umkehr techniques. But, solar cycle effects may be present in the UV, Umkehr and SBUV instruments and long-term temperature trends may affect any of the data sources in various ways.

The Differential Absorption Lidar (DIAL) is also an efficient but relatively expensive technique of measuring the vertical distribution of ozone. In this technique, laser light is transmitted at two wavelengths, one corresponding to a strong absorption of the target molecule and the other to a nearby wavelength having a weak absorption. Lidar measurements of ozone can reach high altitudes around 50 km. Lidar has also been used

to measure NO₂ (Fredriksson and Hertz 1984). The main limitations of the DIAL technique are (1) to limit the number of species, (2) the complexity of both hardware and software are needed to analyse the data. Some of the important constituents involved in the ozone destruction cycles are very difficult to measure in the atmosphere due to their low concentration, or rapidly changing altitude dependent concentration. No single existing ozone profiling instrument or technique is capable of measurements at all altitudes. Ground-based twilight spectroscopy is extensively used for the vertical distribution of O₃ and NO₂ from their SCD measurements in the atmosphere (McKenzie *et al* 1991; Preston *et al* 1997, 1998; Londhe *et al* 1999). Twilight measurements are sensitive to detect trace species because of the enhancement in the air mass factors during twilight period. Preston *et al* (1997) have retrieved vertical profiles of NO₂ from slant columns using ground based UV-visible spectrometer by a sequential estimation using a forward model that consists of a stacked box photochemical model and a radiative transfer model. Profiles of NO₂ obtained by this model are in good agreement with balloonsonde observations in the altitude range 10–35 km.

Method of the data analysis is an important factor for better measurements of the atmospheric trace gases. By utilizing the fine structure of the molecular absorption (absorption cross section) in the visible spectral region, data are analyzed by the differential optical absorption spectroscopy (DOAS) method. The main advantage of this method is that it allows measurements of several different trace-gas species simultaneously (Solomon *et al* 1987; Otten *et al* 1998). Twilight spectroscopy can be efficiently used to monitor long-term changes of different atmospheric species. Thus, ground-based measurement techniques are inexpensive compared to others, can be operated year-round and can be deployed at a large number of sites and profiles derived from them can extend down the troposphere (Preston *et al* 1997). This discussion provides information as to the suitability of data sources, characterization and the sensitivity of the method in validating the measurements. Finally, we validate our method by comparison with the profiles measured by Umkehr and balloon-borne observations.

4.1 Vertical profiles of O₃

The O₃ vertical distributions are retrieved from the set of SCDs measured over a range of SZAs (87–91.5°) during morning twilight using the Chahine iteration method. This method minimizes the difference between observed and recalculated slant column values to determine the optimum

solution profile (McKenzie *et al* 1991; Londhe *et al* 1999).

Figure 2 shows the result of dividing the SCDs by the altitude dependent AMFs for 9 January 2001 at Pune, assuming the entire column to be located within each of the 5 km intervals. This figure is constructed to see where the bulk of ozone resides in the atmosphere. Diurnal variations in ozone are small, so that if the slant column amounts of ozone at twilight are divided by the correct geometric enhancement factors, a constant vertical column should result. The first two layers (0–5 km and 5–10 km) show large increases in vertical columns with SZAs. This is because the AMFs for the first two layers are very low and are almost constant with SZAs but SCDs always increase exponentially with SZAs. For heights around 20–25 km the deduced vertical columns remain approximately constant, suggesting that the bulk of the columns lies near 20–25 km (McKenzie *et al* 1991).

Figure 3 shows the comparison between ozone profiles retrieved by the Chahine iteration method and profiles obtained by the Umkehr method on 9 January, 18 February, 14 March, 22 April, 7 May and 6 December 2001. The data of Umkehr profiles are taken from the site http://www.woudc.org/data_e.html of World Ozone Data Center to make comparison with our vertical profiles. Umkehr data are averaged over about 5 km interval. The abscissa is the column amounts in units of 10¹⁷ molecules cm⁻² retrieved within each 5 km layer. It is seen from figure 3, that the ozone vertical profiles retrieved by Chahine iteration method and Umkehr method, are well matched. Similarly, this figure also shows a comparison between the ozone profiles retrieved by Chahine iteration method and measured directly by sonde, which are integrated over each 5 km interval. For this, depending on the availability of ozonesonde data, the days 9 January and 15 May 2002 are selected for the comparison of vertical profiles. These vertical profiles also matched well and show similar trends at all layers except at the third layer which is near the tropopause level. The retrieved profiles show a maximum column amount in the layer 20–25 km. The concentrations in the layer 25–30 km are seen to be slightly larger than concentrations in the layer 15–20 km. The retrieved vertical profiles of O₃ have a maximum column amount of 17.7 × 10¹⁷ molecules cm⁻² on 9 January, 19.2 × 10¹⁷ molecules cm⁻² on 18 February, 18.7 × 10¹⁷ molecules cm⁻² on 14 March, 19.7 × 10¹⁷ molecules cm⁻² on 22 April, 21.5 × 10¹⁷ molecules cm⁻² on 7 May and 18.3 × 10¹⁷ molecules cm⁻² on 6 December 2001, and 18.8 × 10¹⁷ molecules cm⁻² on 9 January and 20 × 10¹⁷ molecules cm⁻² on 15 May 2002 in the 20–25 km layer.

Figure 2. The twilight progression of vertical column ozone at Pune on 9 January 2000 (day 375), derived from slant column measurements, assuming all the ozone to be located within each of the specified 5-km intervals.

Figure 4 shows the agreement between the observed and recalculated slant columns for the above-mentioned days. The observed SCDs are directly obtained from the scattered light intensity observations collected by spectrometer and recalculated slant columns are the model calculated values deduced from retrieved vertical profiles for morning twilight hours. The fitting is excellent. The maximum number of iterations are shown in each figure at the end point of the curves.

For the sake of comparison TCDs derived for few days using different methods, i.e., vertical profile method, calculated at 90° SZA, measured from Dobson spectrophotometer, obtained from Umkehr method and TOMS values are shown in table 1. TCDs retrieved from vertical profiles and TCDs collected from Dobson spectrophotometer are compared and they are found to be in good agreement.

Figure 5 shows the daily variation of TCDs, stratospheric column densities and tropospheric column densities of O₃ during the period 2000–2003. Here, TCDs of O₃ are derived from vertical profile by integrating the concentration of O₃ for all the 10 layers. Stratospheric column densities are obtained by adding the column amounts of 4 to 10 layers, where each layer is assumed to be a homogeneous layer with uniform extension of 5 km. Similarly, a sum of the first three layers represents tropospheric column densities. Minima of TCD values averaged over

winter months (December and January) are observed to be 6.2×10^{18} molecules cm⁻² in 2000–2001, 5.9×10^{18} molecules cm⁻² in 2001–2002 and 6.07×10^{18} molecules cm⁻² in 2002–2003. TCDs show high values in the months May and June. Therefore, summer maxima considered here are calculated by averaging the values of these months and maxima in TCD values are observed to be 8.1×10^{18} molecules cm⁻² in 2000, 8.02×10^{18} molecules cm⁻² in 2001, 8.4×10^{18} molecules cm⁻² in 2002 and 8.3×10^{18} molecules cm⁻² in 2003. Total column, stratospheric column and tropospheric column densities are maximum in May and June (summer), and minimum in December and January (winter) months for all the years. It can also be seen from this figure that daily stratospheric column densities follow the same pattern of the TCDs of O₃. Similar variations are seen in tropospheric column density also. The gaps in the figure show the non-availability of the data. The daily TCD values of ozone obtained by using ground-based spectroscopic data and TOMS data during the period 2000–2003 are shown in figure 6. The daily TCD values obtained by ground-based spectroscopic observations show more scatter than the TOMS measurements but they follow the similar seasonal trend.

Figure 7 shows the ozone densities in the first layer obtained by profiles (i.e., column density

Figure 3. Comparison between ozone profiles retrieved at Pune at sunrise and Umkehr profiles. The abscissae are the column amounts in units of 10^{17} molecules cm^{-2} retrieved within each 5-km layer.

from surface to 5 km) and surface ozone integrated up to 5 km collected at early morning by O_3 analyzer, which is installed at the Institute at Pune. These surface ozone measurements available for June 2002–June 2003 are used to compare with the column densities of first layer of the retrieved profiles, which are obtained from vertical profiles using spectrometer data carried out over Pune. Density of first layer averaged over May and June months during the year 2002 is 25 DU and surface ozone measured by O_3 analyzer integrated from surface to 5 km which is assumed to be homogeneous in this layer, is equivalent to 29 DU. Average value of December and January months of O_3 is 14 DU obtained for first layer during 2002–2003 and by O_3 analyzer it is 18 DU. Similarly, in 2003, ozone density in the first layer averaged over May and June months is 26 DU, and measured by O_3 analyzer is 32 DU. Thus, for the first

layer (0–5 km), the difference between the densities obtained by O_3 analyzer and iterative method are found to vary from 13 to 23% during the years 2002–2003. From this comparison, it is found that the density values obtained for the first layer of the atmosphere (0–5 km) by Chahine iteration method using spectroscopic observations and the values obtained by ozone analyzer by integrating surface ozone up to 5 km are in good agreement. It should be noted here that the sensitivity of the technique to this lower layer is poor compared to that in the stratosphere. The initial guess profile used in the retrieval of vertical profile of O_3 had a constant mixing ratio with altitude. Gaussian initial profile of half width 10 km, centered at 25 km is used in the model, which follows mostly stratospheric profile. Thus, inaccurate initial guess profile will affect the retrieved profile, especially in the upper stratosphere and lower troposphere.

Figure 4. Observed slant column densities of O₃ during twilight compared with recalculated slant column densities based on the retrieved profiles to see the fitting errors in derived profiles.

Also, the derived enhancement factors are sensitive to errors in the tropospheric contribution, which may give the uncertainties.

4.2 Vertical profiles of NO₂

The NO₂ vertical distributions are retrieved from the set of NO₂ slant column densities measured over a range of 87 to 91.5° SZAs during morning twilight hours using Chahine iteration method (McKenzie *et al* 1991; Londhe *et al* 1999). The AMFs, calculated for SZA between 87° and 91.5° at each 0.5° SZA for 10 layers are used to retrieve NO₂ vertical profiles. As an example, the vertical profiles of NO₂ retrieved on 9 January, 18 February, 14 March, 22 April, 7 May and 6 December 2001 are depicted in figure 8 in which abscissa shows the column amounts in units of 10¹⁴ molecules cm⁻²

retrieved within each 5 km layer from surface to 50 km in the stratosphere. The profiles are linearly interpolated at intermediate heights. The profiles show the maximum column amount in the layer 20–25 km. The retrieved vertical profiles of NO₂ have maximum column amounts in this layer and they are: 2.8 × 10¹⁴ molecules cm⁻² on 9 January, 5.6 × 10¹⁴ molecules cm⁻² on 18 February, 8 × 10¹⁴ molecules cm⁻² on 14 March, 9.4 × 10¹⁴ molecules cm⁻² on 22 April, 10.1 × 10¹⁴ molecules cm⁻² on 7 May and 6.6 × 10¹⁴ molecules cm⁻² on 6 December during the year 2001.

Figure 9 shows observed, and recalculated SCDs of NO₂ obtained by using vertical profiles for the above days of range 87–91.5° SZA. Comparison shows the good agreement between the recalculated and observed slant columns. Fitting errors

Table 1. Total column density (TCD) of O₃ derived from different methods.

Date (year 2001)	Day no.	TCD from profile (molecules cm ⁻²)	TCD at 90° SZA (DU)	TCD from Dobson obs. (DU)	TCD from Umkehr profile (DU)	TCD from TOMS (DU)
9 January	375	6.56×10^{18} (244 DU)	250	247	240	256
18 February	415	6.67×10^{18} (248 DU)	243	246	247	241
14 March	439	6.75×10^{18} (251 DU)	254	259	255	271
22 April	478	7.39×10^{18} (275 DU)	282	278	275	281
7 May	493	7.72×10^{18} (287 DU)	280	284	282	290
6 December	706	6.45×10^{18} (240 DU)	238	242	233	238

Note: 1 January 2000 is considered as day number 1, DU = 2.69×10^{16} molecules cm⁻².

Figure 5. Daily variations of O₃ TCD, stratospheric column and tropospheric column density retrieved from vertical profiles at morning twilight hours during the period 2000–2003.

are shown in each curve. Table 2 shows the comparison made between TCDs of NO₂ obtained by vertical profile and those measured at 90° SZA.

Figure 10 shows the daily variations of total column, stratospheric and tropospheric column densities of NO₂ derived by vertical profiles during the period 2000–2003. It is also evident from this figure that similar variations are observed in total column, stratospheric column and tropospheric column densities of NO₂ during this period. These columns are observed to be maximum in summer and minimum in winter and TCD values vary from 0.51×10^{15} to 1.01×10^{16} molecules cm⁻². In summer months, TCDs (average of May and June) of NO₂ are observed to be 6.5×10^{15} in 2000, 7.3×10^{15} in 2001, 8.2×10^{15} in 2002 and 9.0×10^{15} molecules cm⁻² in 2003, whereas

the minima in winter (average of December and January) are 1.5×10^{15} in 2000–2001, 2.1×10^{15} in 2001–2002 and 2.3×10^{15} molecules cm⁻² in 2002–2003. In the troposphere, maxima of NO₂ density observed are: 1.1×10^{15} in 2000, 1.2×10^{15} in 2001, 1.44×10^{15} in 2002 and 1.46×10^{15} molecules cm⁻² in 2003. The study has revealed that maxima of total column and stratospheric column density are increasing per year by an order of 8×10^{14} molecules cm⁻², i.e., by a factor of 1.12. Tropospheric column densities also show an increasing trend during these years. Lauer *et al* (2002) have reported the seasonal variation of the tropospheric NO₂ column amounts using five-year climatological averages for selected special domains with global coverage, which are retrieved from Global Ozone

Figure 6. Daily variations of O₃ TCD and TOMS values during the period 2000–2003.

Figure 7. Ozone densities in the first layer (i.e., column density from surface to 5 km) obtained by spectrometer and collected from O₃ analyzer at Pune.

Monitoring Experiment (GOME) satellite measurements. These measurements show maximum tropospheric column amount of NO₂ in northern summer months and minimum column amount in northern winter months over the African domain. Similar seasonal trend is observed in our

tropospheric column amounts of NO₂ over the tropical station Pune. The high values of NO₂ in the summer may be attributed to the high lightening activity while in winter months lightening activity is at minimum and hence the reduction of NO₂ (Lauer *et al* 2002). Figure 11 shows the NO₂

Figure 8. Altitude profiles of NO_2 retrieved at Pune at sunrise on 9 January, 18 February, 14 March, 22 April, 7 May and 6 December 2001. The abscissae are the column amounts in units of 10^{14} molecules cm^{-2} retrieved within each 5-km layer.

column densities in the first layer (i.e., column density from surface to 5 km layer). The density trend in the first layer is found to increase per year by a factor of 1.13 during period 2000–2003.

The following fact may give the possible explanation for inter- and intra-annual trends observed in the troposphere and stratosphere in the concentrations of O_3 and NO_2 . Here, twilight chemistry has not been taken into account while calculating the AMFs. The initial profile used to find the vertical distributions of the gases is assumed to be gaussian in nature. The gaussian profile shows low concentrations of O_3 and NO_2 in the troposphere. The intensity data of the morning twilight are collected by the ground-based spectrometer when the pollution is at minimum and these data are used to calculate tropospheric and stratospheric counterparts of O_3 and NO_2 column concentrations.

McKenzie *et al* (1991) have used the Chahine iteration method to retrieve the vertical profiles of O_3 and NO_2 at Lauder, New Zealand ($45^\circ S, 170^\circ E$). Their results show a similar trend in the recalculated column amounts of NO_2 in the vertical (TCD) and in the retrieved tropospheric

vertical columns of NO_2 , during the year 1987. In the case of NO_2 , McKenzie *et al* (1991) have reported that the tropospheric pollution distorts the shape of the vertical profiles of NO_2 and the column concentrations of NO_2 in the troposphere. They have also reported that tropospheric NO_2 columns are lower than the stratospheric columns. Surface and total columns ozone were measured at Delhi ($28.7^\circ N, 77.2^\circ E$) using IR-spectro-radiometer during 1992–1993 and 1994–1995 (Ghosh *et al* 2000). These observations at Delhi showed minima of ozone in November and January and maxima in March during these years. Furthermore, a similar trend is observed in surface and total column ozone at Delhi during these years. Lal *et al* (1993), have evaluated total vertical columns of O_3 and NO_2 at Ahmedabad ($23^\circ N, 72^\circ E$) using visible absorption spectroscopy, which showed minima of O_3 in December 1989 and minima of NO_2 in December 1989, and January 1990. Similarly, seasonal and annual trends observed in the TCDs of NO_2 over Pune ($18^\circ 31', 73^\circ 51'$) are also in good agreement with the polar ozone and aerosol measurement (POAM) observations made

Figure 9. Observed slant column densities (SCDs) of NO₂ during twilight compared with recalculated SCDs based on the retrieved profiles to see the fitting errors in the derived profiles.

Table 2. Total column density (TCD) of NO₂ derived from different methods.

Date (year 2001)	Day no.	TCD from vertical profile (molecules cm ⁻²)	TCD at 90° SZA observation (molecules cm ⁻²)
9 January	375	1.21×10^{15}	1.16×10^{15}
18 February	415	2.07×10^{15}	1.91×10^{15}
14 March	439	3.10×10^{15}	3.02×10^{15}
22 April	478	3.73×10^{15}	3.41×10^{15}
7 May	493	4.10×10^{15}	4.31×10^{15}
6 December	706	2.50×10^{15}	2.13×10^{15}

Note: 1 January 2000 is considered as day number 1.

at Kiruna, Sweden (67.8°N,20.4°E) during the period 1998–2000 (Randall *et al* 2002). Thus, variations in the column abundances of O₃ and NO₂ in the different layers of the atmosphere at Pune are in good agreement with the results of the other researchers discussed above.

4.3 Error budget

The errors in the slant column density (SCD) of trace gases come from instrumental noise, uncertainties in cross-sections and interpolation error

during analysis. The random error in the instrument is introduced due to the dark current, light intensity source, scintillation effect and cloud movements. The spectrometer is able to scan 4800 spectra in a single observation at the rate of 40 spectra per second. The random noise in the instrument is reduced to range between 2 and 1% by averaging these multiple spectra. The spectrometer measures zenith scattered light which is elastically scattered by air molecules and particles in the zenith direction. The error generated by ‘filling in’ of absorption features by Raman scattered light is

Figure 10. Daily variations of NO₂ TCDs, stratospheric column and tropospheric column densities retrieved from vertical profiles at morning twilight hours during the period 2000–2003.

Figure 11. NO₂ densities in the first layer (i.e., column density from surface to 5 km) during the period 2000–2003.

3–6% in case of NO₂ and 1–3% for O₃. The uncertainty in cross-sections is 2.6% for ozone and 2.4% for NO₂. Measurement errors in the observed SCDs are estimated to be 2–3% for O₃ and 3–5%, for NO₂ due to the residual in the DOAS spectral fit. Some

unknown species, which are not included in the spectral fit, may give the uncertainties in the measurements. The root-sum-square error calculated from these various error sources is approximately 5–8% in SCDs of NO₂ and 3–6% in SCDs of O₃.

The errors are introduced in the vertical column density for larger solar zenith angles than for normal geometries due to decreased instrument signal-to-noise, variations in the ozone particles, large temperature variations and decreased sensitivity of tropospheric ozone. In the case of NO_2 , rapidly changing photochemistry at twilight plays an important role in the retrieval process that is not considered in the present study. Also the uncertainties arise in the calculation of vertical column conversion procedure as a result of inaccuracies in the AMF calculations, hypothesis of constant vertical profile and aerosol profile. The scattering model considered here assumes cloud free condition with no background aerosols. The effects of multiple scattering, which are important, especially in the troposphere at larger SZAs, are ignored in the calculation of AMFs. The error associated with calculated layerwise AMFs due to approximations in the RT model is about 1–2% for O_3 and 3–5% for NO_2 . These errors contribute to the total error in retrieved vertical profiles of O_3 and NO_2 at all the altitudes. Overall error in the vertical profiles is estimated to be 3–6% for O_3 and 6–9% in the case of NO_2 .

The relative errors are defined as errors that can vary for two measurements for the same location. In order to make quantitative comparison it is more useful to examine relative error (percentage difference) with other instruments for identifying weakness in a measurement. The ozone profiles retrieved by our ground-based spectrometer are compared with Umkehr and ozonesonde observations. The difference in vertical profiles of O_3 and NO_2 obtained by different methods is observed to change with altitude and can be evidenced in the figures 3 and 8 respectively. The percentage difference (relative error = $\frac{\text{Retrieved} - \text{Umkehr}}{\text{Umkehr}} \times 100$) between retrieved and Umkehr profile seems to vary from –4 to 6% in the tropospheric layer (0–15 km). In the lower stratosphere (15–30 km), percentage difference varies from –6 to 9% except on 9 January 2001 it is –17% in 15–20 km layer and 30% in 25–30 km layer and on 14 March it is –14% in 15–20 km layer. The percentage difference on most of the days varies between 1 and 2% in the upper stratosphere, i.e., in the altitude region 30–50 km except on 18 February 2001 it varies from –13 to 9%. The initial guess profiles used in all the retrievals had a constant mixing ratio with altitude that gives larger relative errors with ozonesondes in the tropospheric ozone column amounts. The ozonesonde data up to 25 km is available for comparison only for 9 January 2002 and 15 May 2002. The percentage difference with ozonesonde on these days is very high and it lies between –50 and 86% in 0–15 km layer and 4 to 43%

in 15–25 km layer. The percentage difference between the TCDs obtained by vertical profiles and from Dobson observations is observed to vary from 1 to 3% on the days given in table 1. Similarly, the TCDs obtained by iteration method differ by 1 to 4% when compared with TCDs obtained by Umkehr method and calculated at 90° SZA. Most of the TCD values of ozone retrieved by using spectroscopic observations differ by $\pm 15\%$ from TOMS observations. The integrated total column amounts (TCDs) obtained from vertical profiles of NO_2 differ by –5 to 9% from the TCDs derived at 90° SZA on the days shown in table 2 except on 6 December 2001 where it differs by 17%.

5. Conclusions

An algorithm developed has been used for retrieving vertical profiles of O_3 and NO_2 from ground-based measurements using the Chahine iteration method. The vertical profiles of O_3 retrieved by this method are in good agreement with Umkehr profiles. The bulk of the column densities is found near 20–25 km and the retrieved concentrations in the layer 25–30 km are found to be slightly larger than concentrations in the layer 15–20 km. The measured and recalculated slant column amounts have been compared, and they are found to be matching well.

The daily TCD values along with stratospheric and tropospheric column densities of O_3 and NO_2 have been derived using their vertical profiles during the period 2000–2003. The total column, stratospheric column and tropospheric column amounts are found to be maximum in summer and minimum in winter season, i.e., they are in the same phase and follow the same seasonal trend. This study reveals that the maxima of total column and stratospheric column densities of NO_2 are increasing per year by the order of 8×10^{14} molecules cm^{-2} . Also, NO_2 densities in the 0–5 km layer are found to be increasing per year by a factor of 1.13 during the period 2000–2003. But, no trend is observed in the maxima of O_3 columns during this period.

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