Atmósfera 20(3), 271-287 (2007)

Study of diurnal and seasonal variation of atmospheric NO_2, O_3, H_2O and O_4 at Pune, India

G. S. MEENA and D. B. JADHAV
Indian Institute of Tropical Meteorology, Pashan, Pune-411008, India
Corresponding author: G. S. Meena; e-mail: gsm@tropmet.res.in

Received March 21, 2006; accepted January 24, 2007

RESUMEN

El estudio de la variación diurna y estacional de los gases traza atmosféricos es esencial para entender nuestra atmósfera. Para esto, en el período 2000-2003 se realizaron observaciones diarias de luz zenital dispersa utilizando un espectrómetro UV-visible. Para observar las variaciones diurnas de NO_2, O_3, H_2O y O_4, se obtuvieron las densidades de columna inclinada (SCD) desde las mañanas (ángulo zenital solar (SZA) = 90°) hasta las tardes (SZA = 90°). Para el estudio de las variaciones estacionales de NO_2 y O_3, se obtuvieron las densidades de columna vertical (VCD) durante el período mencionado. Para los datos de VCD de NO_2 y O_3, se encontró una correlación positiva de $r = 0.72$ para las mañanas y de $r = 0.79$ para las tardes. Se compararon las observaciones de satélite con las espectroscópicas y se observó una buena correlación. Los valores más altos de VCD para NO_2 y O_3 aparecen en los meses de verano (mayo y junio) y los más bajos en los meses de invierno (diciembre y enero). Las VCD vespertinas del NO_2 son más altas que las matutinas. Para la ciudad de Puna (18°32' N, 73°51' E) se encontró un cambio estacional interesante: las tasas vespertina/matutina (PM/AM) de NO_2 y de las temperaturas máximas/mínimas son mayores en los meses de invierno que en los de verano para todo el período de estudio. En los meses de invierno la tasa PM/AM del NO_2 llega hasta 3.8 y la menor para los meses de verano es de 1.25. Durante el día, el N_2O_5 puede fotolizarse para regenerar NO_2, lo que se refleja en las tardes. En el invierno las noches son más largas, por lo que durante ellas la conversión de NO_2 en N_2O_5 es mayor y los valores de NO_2 son menores en las mañanas, lo que produce una tasa PM/AM elevada. La tasa PM/AM del O_3 es ligeramente más elevada en los meses de invierno que en los de verano.

ABSTRACT

Study of diurnal and seasonal variation of atmospheric trace gases is essential to understand our atmosphere. For this, daily zenith-sky scattered light observations have been made by UV-visible spectrometer during the period 2000-2003. Slant column densities (SCD) from morning (solar zenith angle SZA = 90°) to evening (SZA = 90°) were retrieved to see the diurnal variation of NO_2, O_3, H_2O and O_4. For the study of seasonal behavior of NO_2 and O_3, vertical column densities (VCD) were retrieved during the above period. For the whole period, NO_2 and O_3 VCD are found in a positive correlation of $r = 0.72$ for the morning data and $r = 0.79$ for the evening data. Satellites borne observations are compared with the spectroscopic observations, which are found in good correlation. It is seen that highest NO_2 and O_3 VCD are found in summer months

(May and June) and lowest in winter months (December and January). Evening NO_2 VCD are found higher compared to morning. There is found an interesting seasonal change that at Pune (18°32′ N, 73°51′ E), the evening-to-morning (PM/AM) ratios of NO_2 as well as temperature maximum/minimum ratios are higher in winter months and lower in summer months during the above period. In winter months NO_2 PM/AM ratio goes up to 3.8 and in summer months lowest ratio is 1.25. During the day, N_2O_5 can be photolyzed to regenerate NO_2, which reflects in the evening hours. In the winter, nights are longest; therefore, during night NO_2 to N_2O_5 conversion is more, hence in the morning NO_2 value will be less that leads to high PM/AM ratio. O_3 PM/AM ratio is slightly higher in winter months compared to summer months.

Keywords: Ozone, nitrogen dioxide, vertical column density, solar zenith angle, diurnal and seasonal variation.

1. Introduction

Tropospheric NO_2 plays a key role in both stratospheric and tropospheric chemistry. In the troposphere the photolysis of NO_2 results in the formation of O_3 (Bradshaw *et al.*, 2000). NO_2 can react with O_3 to form the nitrate radical (NO_3), which is a strong oxidant and plays an important role in NO_x polluted areas at night (Wayne, 1991).

Ozone is one of the most extensively measured trace gases in the atmosphere. Column amounts of O_3 vary with season and altitude. WMO (1990a) has reported that the highest ozone abundances are found at high latitudes in winter and early spring, while the lowest values are located in the tropics. Most ozone is produced at low latitudes, where the solar irradiance is highest. Large day-to-day variations were found to be more at higher latitudes. Latitudinal and seasonal distributions of NO_2 have been conducted by Kreher *et al.* (1995) and by Senne *et al.* (1996). Daily/seasonal variations in vertical column densities (VCD) of NO_2 and O_3 have been studied using spectroscopic observations (Syed *et al.*, 1981; McKenzie and Johnston, 1982; Bhonde *et al.*, 1992; Solomon *et al.*, 1992; Kondo *et al.*, 1994; Gil *et al.*, 1996; Nichol *et al.*, 1996; Koike *et al.*, 1999; Jadhav *et al.*, 1999; Meena *et al.*, 2004).

Water vapour in the lower stratosphere is a very effective greenhouse gas. The atmospheric water vapour content responds to changes in temperature, microphysical processes and the atmospheric circulation. Water vapour concentration varies substantially in both the vertical and horizontal (Jayaraman and Subbaraya, 1988). Clouds are intimately connected to the water vapour pattern, as clouds occur in connection with high relative humidity, and cloud processes in turn affect the moisture distribution. In the atmospheric physics, O_4 is also an absorber of solar radiation (e.g., Pfeilsticker *et al.*, 1997; Solomon *et al.*, 1998) and toll to infer atmospheric photon path lengths, and cloud heights (e.g., Erle *et al.*, 1995). Pfeilsticker *et al.* (1997) have reported that O_4 band does not saturate for cloudy skies. Therefore, O_4 can be considered to identify the clouds, which affect the measurements.

In this paper, for the study of diurnal variation differential slant column densities (SCD) of NO_2, O_3, H_2O and O_4 are presented for few days from morning to evening. For the study of diurnal and seasonal variation of NO_2 and O_3, UV-visible spectrometer is operated during the period 2000-2003. Study of diurnal and seasonal variations of NO_2 and O_3 have been made and daily morning/evening variations in NO_2 and O_3 are discussed. The evening to morning (PM/AM) ratios of NO_2 and O_3 are discussed with maximum/minimum temperature ratios during this period. Spectroscopic observations are compared with satellite borne Nimbus-7 Total Ozone Mapping Spectrometer (TOMS) observations.

2. Methodology

Zenith scattered light spectra recorded with the spectrometer are analyzed using differential optical absorption spectroscopy (DOAS) technique (Noxon, 1975; Solomon *et al*., 1987; Pommereau and Goutail, 1988; Bhonde *et al*., 1992; Platt, 1994; Londhe *et al*., 1999; Jadhav, 2002; Meena *et al*., 2003; Bhosale *et al*., 2004) to determine vertical column amounts of atmospheric trace gases such as O_3 and NO_2. The DOAS analysis algorithm uses the log ratio of a twilight spectrum to midday one, i.e. in determination of the slant column amount; Lambert-Beer's law is used. In the log ratio spectrum of wavelength range 462-498 nm; NO_2, O_3, H_2O and O_4 have their absorption signatures. SCD of these gases are derived simultaneously by matrix inversion method. To retrieve vertical column density (VCD), it is necessary to divide the SCD by a factor. For large solar zenith angle (SZA) sunlight passes nearly tangentially through the atmosphere before being scattered down to ground and the absorption path enhances by a factor called air mass factor (AMF).

AMF for different SZA are calculated using single scattering radiative transfer (RT) model (Solomon *et al*., 1987; Meena *et al*., 2003). In order to retrieve VCD, there are two approaches. The first approach is to retrieve ozone vertical columns that plots the observed differential slant column densities (SCD_{diff}) against the corresponding AMF (called a Langley plot). Then the slope of the line is equal to the VCD, as shown in equation (1). The Y-intercept should be equal to the negative of the column density of an absorber in the reference spectrum (RCD):

$$SCD_{diff}(\theta) = VCD \times AMF(\theta) - RCD \tag{1}$$

Equation (1) can be rearranged to solve for VCD at particular SZA, θ:

$$VCD(\theta) = (SCD_{diff}(\theta) + RCD) / AMF(\theta) \tag{2}$$

In equation (1) and (2), AMF(θ) is the air mass factor at SZA θ.

The second approach is based on the assumption that the vertical column in the background measurement is the same as in the actual measurement, and the differences in vertical columns are only due to changes in light path. With this assumption, equation (1) can be written as:

$$SCD_{diff}(\theta) = VCD \times AMF(\theta) - VCD \times AMF(\theta_0)$$

or

$$VCD = SCD_{diff}(\theta) / [AMF(\theta) - AMF(\theta_0)] \tag{3}$$

where θ_0 is the SZA of reference spectrum. For the study of seasonal variations O_3, VCD are derived at 90° SZA using equation (2). The use of equation (1), and the Langley plot method is less appropriate for NO_2 because NO_2 concentrations change during twilight. Thus for NO_2, equation (3) can be applied at 90° SZA.

3. Observations

Zenith-sky spectra (462-498 nm) are recorded daily by UV-visible spectrometer. Full day observations, from morning (SZA = 90°) to evening (SZA = 90°) on 18, 19, 21, 22 and 23 October, 2000, have been carried out to see the diurnal variation of trace gases such as NO_2, O_3, H_2O and O_4. Daily morning/evening observations have been made to see the seasonal variations of NO_2 and O_3 at Pune (18°32´ N, 73°51´ E) during the period 2000-2003. To retrieve the RCD, plots of SCD_{diff} against a set of the corresponding AMF (Langley plot) are needed. Hence, the set of AMF (SZA) for respective SZA is acquired by RT model. For the sake of comparison, data of O_3 VCD from Dobson instrument of Pune station are collected from the web site http://www.msc-smc.ec.gc.ca/woudc/index_e.html of World Ozone Data Centre (WODC), and TOMS data for the same station are collected from http://jwocky.gsfc.nasa.gov/eptoms/ep.html. Daily maximum/minimum temperature is collected from Indian Daily Weather Report (IDWR) reported by Indian Meteorological Department to understand the variation in NO_2 PM/AM ratio.

4. Results and discussion

4.1 Diurnal variation

As an example, full day observations on 18, 19, 21, 22 and 23 October 2000 have been made for the study of diurnal variations of NO_2, O_3, H_2O and O_4. Figures 1a and b shows the SCD_{diff} of NO_2 and O_3, respectively, with SZA for the above mentioned days. Similarly, H_2O and O_4 SCD_{diff} are shown in Figure 1c and d. Here, SCD_{diff} is the difference of the SCD in observed spectrum of particular SZA and reference spectrum of 30° SZA. Therefore, SCD_{diff} at 30° SZA will be zero for all the gases. In both the figures, SCD_{diff} of above gases are smoothly increasing with increasing SZA due to increasing atmospheric light paths approaching higher SZA.

From Figure 1a, it is seen that evening NO_2 SCD_{diff} are higher than morning SCD_{diff} at same SZA. At 70° SZA, percentage difference between evening and morning NO_2 SCD_{diff} varies from 50 to 57%; similarly, at 80° SZA percentage difference varies from 59 to 66% between evening and morning NO_2 SCD_{diff}. From Figure 1b, it is seen that O_3 SCD_{diff} at morning and evening hours are almost similar. O_3 SCD_{diff} are increasing with SZA due to increasing absorption path at higher SZA. From Figure 1c and d, it has been seen that H_2O and O_4 SCD_{diff} variations are more between the selected days compared to NO_2 and O_3. Water vapour has large variability in the troposphere and stratosphere. The major absorption is in the lower layer of the atmosphere. Hence, the zenith dependence of wather vapour variability is different compared to other three gases. The atmospheric content of this compound responds to changes in temperature, microphysical processes and the atmospheric circulation. Water vapour concentration varies substantially in both the vertical and horizontal. Clouds are intimately connected to its pattern, as clouds occur in connection with high relative humidity, and cloud processes in turn affect the moisture distribution. Table I shows SCD_{diff}

of NO_2, O_3, H_2O and O_4 at morning (AM) and evening (PM) 90° SZA for selected days. From Table I, it is seen that the evening NO_2 values are almost double of morning NO_2 values at 90° SZA. The percentage difference between evening and morning NO_2 SCD_{diff} values varies from 78 to 107% at 90° SZA during those days. These higher values of NO_2 in the evening particularly at SZA greater than 85° compared to morning NO_2 may have occurred due to increased rate of NO-NO_2 conversion and decreases in the rate of photolysis of NO_2 during evening twilight period. From Table I, it has been seen that evening densities of O_3 are 1-5% higher than morning densities at 90° SZA during those days. H_2O SCD_{diff} at evening 90° SZA are found to be 2-11% higher than morning SCD_{diff} of same SZA. Similarly, O_4 SCD_{diff} are 0-26% higher than morning SCD_{diff} at evening 90° SZA. On October 19, O_4 SCD_{diff} at evening is 26% higher than morning. It is also seen that on this day H_2O SCD_{diff} at evening 90° SZA is 11% higher than morning compared to other days. These higher values of O_4 and H_2O on October 19, at evening 90° SZA may be due to cloud layer occurred at evening hours. Meena *et al.* (2004) have been noticed that more effects of clouds are seen in increased absorption of tropospheric species like H_2O and O_4, which are good indicative of the increased absorption path lengths due to multiple Mie-scattering inside clouds.

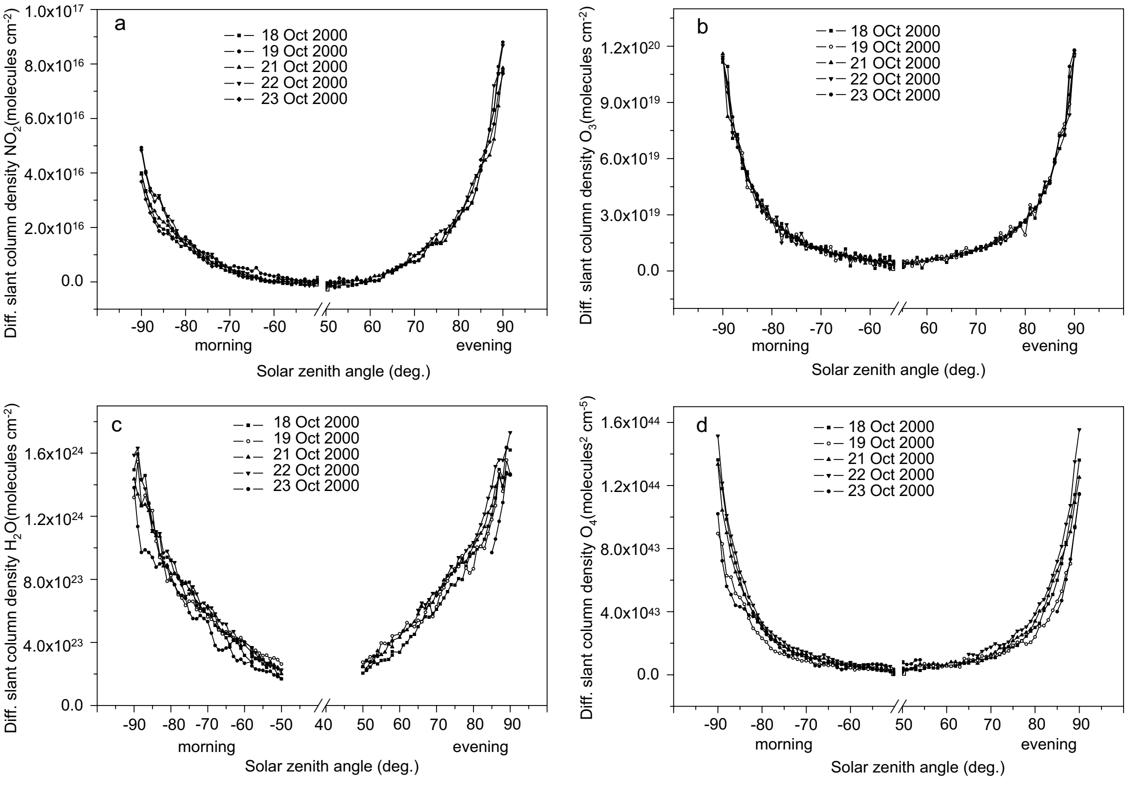

Fig. 1. a) Differential slant column densities of NO_2 with solar zenith angles, b) Same as a) but for O_3, c) Same as a) but for H_2O, d) Same as c) but for O_4.

Table I. Differential slant column densities (SCD_{diff}) of NO_2, O_3, H_2O and O_4 at morning (AM) and evening (PM) 90° SZA.

Day of October 2000			18	19	21	22	23
SCD_{diff} at 90° SZA (molecules cm^{-2})	NO_2	AM	4.00×10^{16}	4.93×10^{16}	3.96×10^{16}	4.82×10^{16}	3.68×10^{16}
		PM	7.73×10^{16}	8.79×10^{16}	7.85×10^{16}	8.68×10^{16}	7.65×10^{16}
	O_3	AM	1.11×10^{20}	1.13×10^{20}	1.15×10^{20}	1.14×10^{20}	1.13×10^{20}
		PM	1.15×10^{20}	1.15×10^{20}	1.16×10^{20}	1.17×10^{20}	1.18×10^{20}
	H_2O	AM	1.49×10^{24}	1.32×10^{24}	1.43×10^{24}	1.59×10^{24}	1.38×10^{24}
		PM	1.62×10^{24}	1.47×10^{24}	1.46×10^{24}	1.73×10^{24}	1.46×10^{24}
	O_4	AM	1.36×10^{44}	8.95×10^{43}	1.33×10^{44}	1.51×10^{44}	1.02×10^{44}
		PM	1.36×10^{44}	1.40×10^{44}	1.25×10^{44}	1.55×10^{44}	1.14×10^{44}

Figure 2 shows the plots of SCD_{diff} vs AMF (Langley plot) of O_3 at evening on October 18, 19, 21 and 22. The correlation coefficients (r) between SCD_{diff} and AMF are 0.99 for 18, 19 and 21 October and 0.98 for 22 October. The correlation coefficients are significant at 1% level. In Figure 2, straight lines are showing the linear fit to the data. From the Langley plots, it is seen that data follow the straight line. According to equation (1), Y intercept gives the slant column amount in reference spectrum and slope of Langley plots gives the VCD, which are listed in Table II. This table, it is seen that the VCD derived by the slope of Langley plots and VCD90 using equation (2) have not much difference. They appear to be in good agreement. VCD derived from our spectrometer at evening 90° SZA are observed to be less by 2 to 10 DU compared to Dobson instrument values (V_{Dob}) and 6 to 22 DU less from TOMS observed values. The percentage difference in VCD derived by Dobson and our spectrometer varies from 0.8 to 4%. Similarly, the percentage difference between VCD obtained from our spectrometer and TOMS varies from 1 to 8% on these days. There are a number of factors contributing to the total error in the VCD. The basic uncertainty of O_3 and NO_2 is given by the random error from the fit. The random error is 1% for O_3 and 2% for NO_2. Uncertainty in cross sections is 1.2% for O_3 and 2.3% for NO_2. Pseudo-random error causing structure in the "filling-in" of absorption features by Raman scattered light is 1% for O_3 and 5% for NO_2. Another factor is that associated with the calculated AMF due to approximations in the RT model, which is 2.7% for O_3 and 5% for NO_2. The root-sum-square error calculated from these various error sources is approximately 3% for O_3 and 8% for NO_2.

4.2 Seasonal variation

Figures 3a and b show the daily VCD of NO_2 and O_3, respectively, obtained in the morning and evening hours during the period May 4, 2000 to May 24, 2003. VCD were derived from SCD at 90° SZA using the AMF of 18.5 for NO_2 and 18.3 for O_3, which were calculated by RT model for 90° SZA. Also, daily ozone values obtained by Dobson spectrophotometer are plotted in Figure 3b for the above period. From Figure 3a, it is seen that maximum NO_2 VCD are found in summer months (May and June) and minimum in winter months (December and January) for all the years.

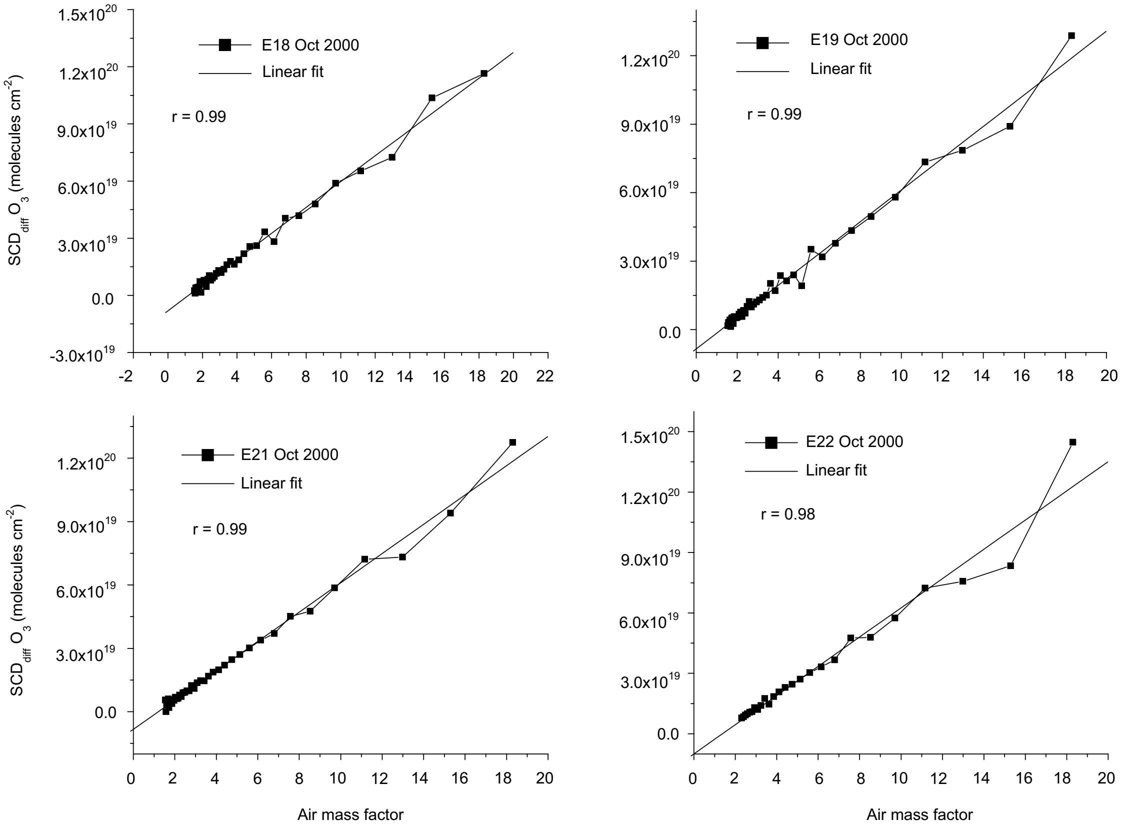

Fig. 2. Langley plots (SCD_{diff} vs. AMF) of O_3 measurement on evening 18, 19, 21 and 22 October 2000.

Table II. Slant column densities (SCD) and vertical column densities (VCD) of O_3 derived by the Langley plots and VCD_{90} using equation (2).

Day No.	Day of the year 2000	Evening SCD_{diff} at 90° SZA molec. cm^{-2}	Y intercept of Langley plots = RCD 30° molec. cm^{-2}	Slope of Langley plots = VCD molec. cm^{-2}	VCD 90° using eq. (2) molec. cm^{-2}	V_{Dob} (DU)	V_{TOMS} (DU)
292	18 Oct	1.15×10^{20}	7.70×10^{18}	6.67×10^{18}	6.69×10^{18} (249 DU)	259	271
293	19 Oct	1.15×10^{20}	7.72×10^{18}	6.73×10^{18}	6.71×10^{18} (250 DU)	256	261
295	21 Oct	1.16×10^{20}	7.79×10^{18}	6.73×10^{18}	6.77×10^{18} (252 DU)	254	258
296	22 Oct	1.17×10^{20}	7.85×10^{18}	6.80×10^{18}	6.83×10^{18} (254 DU)	256	273
297	23 Oct	1.18×10^{20}	7.91×10^{18}	6.82×10^{18}	6.88×10^{18} (256 DU)	258	272

V_{Dob} and V_{TOMS} are ozone vertical column collected from Dobson and TOMS instrument, respectivly. January 1, 2000 is considered as day number 1, 1 DU = 2.69×10^{16} molecules cm^{-2}.

Maximum NO_2 VCD (average of May and June) and minimum NO_2 VCD (average of December and January) of morning and evening hours are listed in Table IIIa. From this table, it is seen that at morning and evening hours, maxima of NO_2 of VCD have an increasing trend during the period 2000-2003. The maximum NO_2 VCD in the morning hours are increasing per year in the order of $0.4 \times 10^{15} - 0.5 \times 10^{15}$ molecules cm^{-2} (i.e., 7-8%) and in evening hours it is increasing 5-6% per year. The percentage difference between maximum NO_2 VCD at morning and evening hours varies from 29 to 42%; similarly, percentage difference between minimum NO_2 VCD at morning and evening hours varies from 150 to 172% during the period 2000-2003. Regarding the NO_2 concentration, it was observed at Pune that two wheelers contribute 74 and cars 20% to the total pollution. The air quality of Pune's surroundings is deteriorating rapidly. Every day hundreds of tons of polluted air are released. Vehicular contribution of Pune's air pollution is approximately 40%. The average air pollution levels in the city are given as: PM_{10} 83 ppm, NO_2 62 ppm and SO_2 37 ppm. The observation station is in upwind and hence the effect of Pune pollution depends upon wind direction. However, the tropospheric contribution will only affect the observations and stratospheric contributions are representative of large circulation patterns.

From Figure 3b, it is seen that maximum O_3 VCD are observed in summer months (May and June) and minimum in winter months (December and January). From the figure it is also seen that morning and evening VCD are in good agreement with Dobson spectrophotometer values throughout the observational period. Maximum O_3 VCD (average of May and June) and minimum O_3 VCD (average of December and January) at morning and evening hours are listed in Table IIIb. From table, it is seen that evening O_3 VCD are higher than morning O_3 VCD. The percentage difference between maximum O_3 VCD at morning and evening hours varies from 3 to 10% and the percentage difference between minimum O_3 VCD at morning and evening hours varies from 2 to 18% during the period 2000-2003. Figure 3c shows correlation between NO_2 and O_3 for morning (AM) and evening (PM) data. For the whole period, a positive correlation of $r = 0.72$ in the morning data and $r = 0.79$ in the evening have been found between NO_2 and O_3 total column amounts.

Figures 4a and b show the daily maximum/minimum temperature and VCD of O_3 obtained by spectrometer and TOMS data during 2000-2003. In Pune, summer goes from early March to June, from November to February Pune has it's winter season, and the monsoon season with good rain from July to October. There were maximum temperature ranges from 40 to 42 °C starting in May and minimum temperature ranges from 5 to 7 °C in December-January during 2000-2003. From Figure 4a, maximum temperature is observed in April and May of averaged 38 °C and minimum temperature is observed in December and January of averaged 11 °C during all the years.

It has been discussed above that maximum NO_2 and O_3 VCD are observed in May and June during all the years, therefore it can be say that NO_2 and O_3 peaks are one month ahead from maximum temperature peaks. A good agreement is seen between O_3 and minimum temperature variations. It is found from Figure 4b that TOMS values are higher than spectrometer values. The TOMS instrument measures UV radiances backscattered by the underlying atmosphere and earth's surface or clouds. The measured radiances are a function of total column ozone, the vertical distribution of that column, solar zenith angle, satellite zenith angle (azimuthal angle and scan angle), and the pressure level and reflectivity of the lower boundary. In clear sky conditions the contribution of backscattered radiation from the atmosphere dominates over the reflected radiation from earth's surface, the effective scattering surface for the backscattered UV radiation to the TOMS instrument is at the middle to upper troposphere (Hudson *et al*., 1995; Klenk *et al*., 1982).

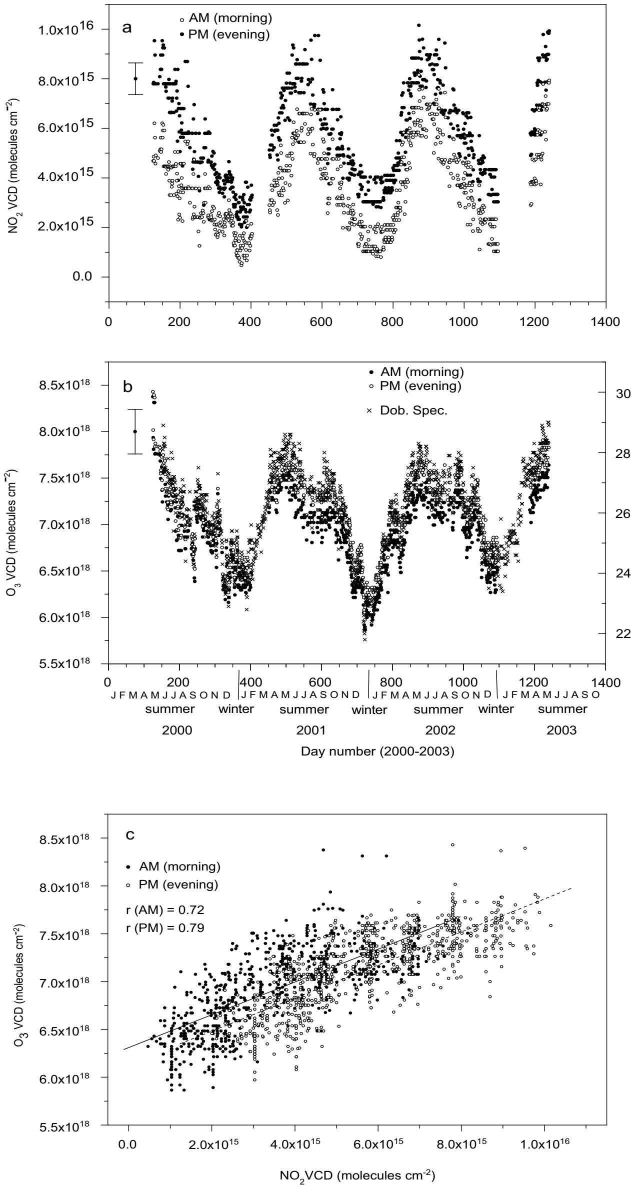

Fig. 3. a) Time series of total column density of NO_2 at sunrise (AM) and sunset (PM) during period 2000-2003, b) Same as a) but for O_3 compared with Dobson spectrophotometer values, c) Correlation between NO_2 and O_3 VCD for AM and PM data.

Table IIIa. Maximum NO_2 VCD (average of May and June) and minimum NO_2 VCD (average of December and January) at morning and evening hours during the period 2000-2003.

Years	Maximum NO_2 VCD in molecules cm^{-2} (average of May and June)		Years	Minimum NO_2 VCD in molecules cm^{-2} (average of December and January)	
	Morning	Evening	- - -	Morning	Evening
2000	5.6×10^{15}	8.0×10^{15}	2000 - 01	1.0×10^{15}	2.5×10^{15}
2001	6.0×10^{15}	8.1×10^{15}	2000 - 02	1.2×10^{15}	3.2×10^{15}
2002	6.5×10^{15}	8.5×10^{15}	2002 - 03	1.1×10^{15}	3.0×10^{15}
2003	7.0×10^{15}	9.0×10^{15}	- - -	- - -	- - -

Table IIIb. Maximum O_3 VCD (average of May and June) and minimum O_3 VCD (average of December and January) at morning and evening hours during the period 2000-2003.

Years	Maximum O_3 VCD in molecules cm^{-2} (average of May and June)		Years	Minimum O_3 VCD in molecules cm^{-2} (average of December and January)	
	Morning	Evening	- - -	Morning	Evening
2000	7.5×10^{18}	8.3×10^{18}	2000 - 01	6.4×10^{18}	7.6×10^{18}
2001	7.4×10^{18}	7.6×10^{18}	2000 - 02	6.1×10^{18}	6.4×10^{18}
2002	7.3×10^{18}	7.6×10^{18}	2002 - 03	6.5×10^{18}	6.7×10^{18}
2003	7.5×10^{18}	7.8×10^{18}	- - -	- - -	- - -

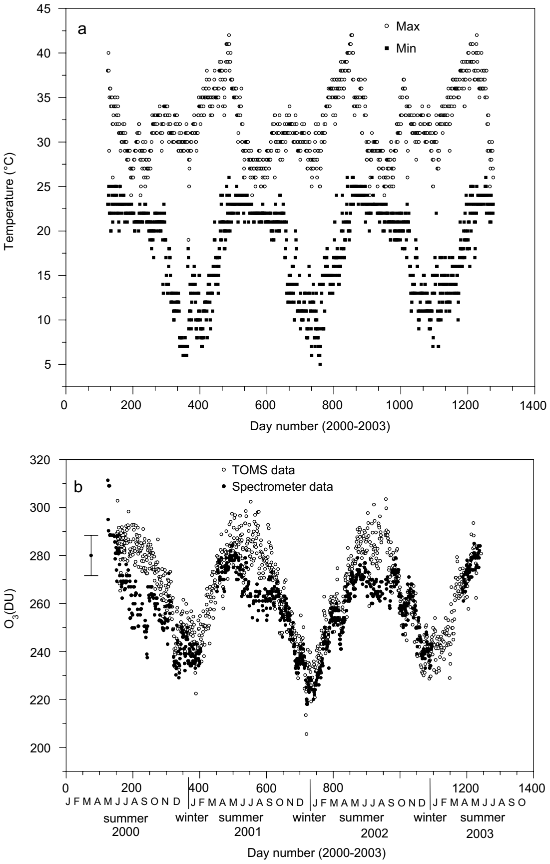

Fig. 4. a) Daily max/min temperature, b) Comparison of spectrometer data and TOMS data of ozone during 2000-2003.

For ozone above the middle to upper troposphere, the TOMS algorithm can retrieve the actual amount of ozone above the effective scattering surface with little error. However, if the assumed ozone profile below the effective scattering surface is different from the actual ozone profile, the retrieval will sense less than the actual deviation because some of the backscattered radiation will not have passed through the middle and lower troposphere. Then, the retrieved total ozone is either overestimated or underestimated depending on whether the assumed ozone amount below the effective scattering surface is less than or greater than the actual ozone amount. In the cloudy sky, incorrect cloud height lead to three errors like errors in the added ozone below clouds and errors in the retrieved ozone above clouds.

The knowledge of ozone and temperature profiles is critical for the calculation of ozone values at higher solar zenith angles. The effect of different profiles on the accuracy of ozone retrievals is an important part. Therefore, the reason of the observed discrepancies may be in the TOMS algorithm, which uses climatological profiles rather than the actual profile at the time of the measurement. High summer ozone concentrations are confined to increased duration of UV-radiation during summer months. Ozone produced in the tropical region gets transported to higher latitudes by the stratospheric mean diabatic circulation. Ozone rich-air during winter moves poleward and downward, which explains the seasonal variations in ozone. Also, day-to-day variability in total ozone is assumed to be caused by changing weather patterns in the troposphere and its effects may extent to the lower stratospheric levels. Ozone has a strong seasonal variation but weak diurnal variation at twilight, with maxima in the summer and minima in the winter. However, the abundance of lower stratospheric ozone is strongly dependent on transport, so that interannual variations in dynamic behavior can also be a source of ozone variability (Hood *et al.*, 1997).

Figures 5a and b show the NO_2 and O_3 evening-to-morning (PM/AM) ratio, respectively, during 2000-2003. Also, Figure 5a shows temperature maximum/minimum (max/min) ratio. Figure 5c shows the correlation between NO_2 PM/AM ratio and temperature max/min ratio during 2000-2003. From Figure 5a, it is found that at Pune the PM/AM ratio of NO_2 density varies from 1.25 to 3.8 during the above period. There is an interesting seasonal change in the PM/AM ratio. NO_2 PM/AM ratios are higher in winter months and lower in summer months for all the years. In winter months NO_2 PM/AM ratio goes up to 3.8 and in summer months lowest ratio is 1.25. From Figure 5a, it is seen that max/min temperature ratios are higher in winter months and lower in summer months during 2000-2003. Decreasing trend is observed in the maxima of both NO_2 PM/AM ratio and temperature max/min ratio in winter seasons during the above period. When the max/min temperature differences are more, NO_2 PM/AM differences are also observed more. The NO_2 PM/AM ratio has been plotted against the temperature max/min ratio with a correlation coefficient of 0.55, which is shown in Figure 5c. Deviation from linearity indicates other processes than pure photochemical and homogeneous chemistry. The NO_2 concentration and its PM/AM ratio is considered to change with the atmospheric temperature in a day/night period.

Temperature of the atmosphere controls the rate of thermal decomposition of N_2O_5 concentrations. N_2O_5 forms during the dark hours and is destroyed by photolysis and thermal decomposition. N_2O_5 concentration is a function of temperature and wavelength. In the winter nights N_2O_5 forms more due to more dark hours and in day time it is photolyzed to produce NO_2, which is reflecting in the evening (PM) hours. Hence, in winter PM/AM ratios are higher than in summer.

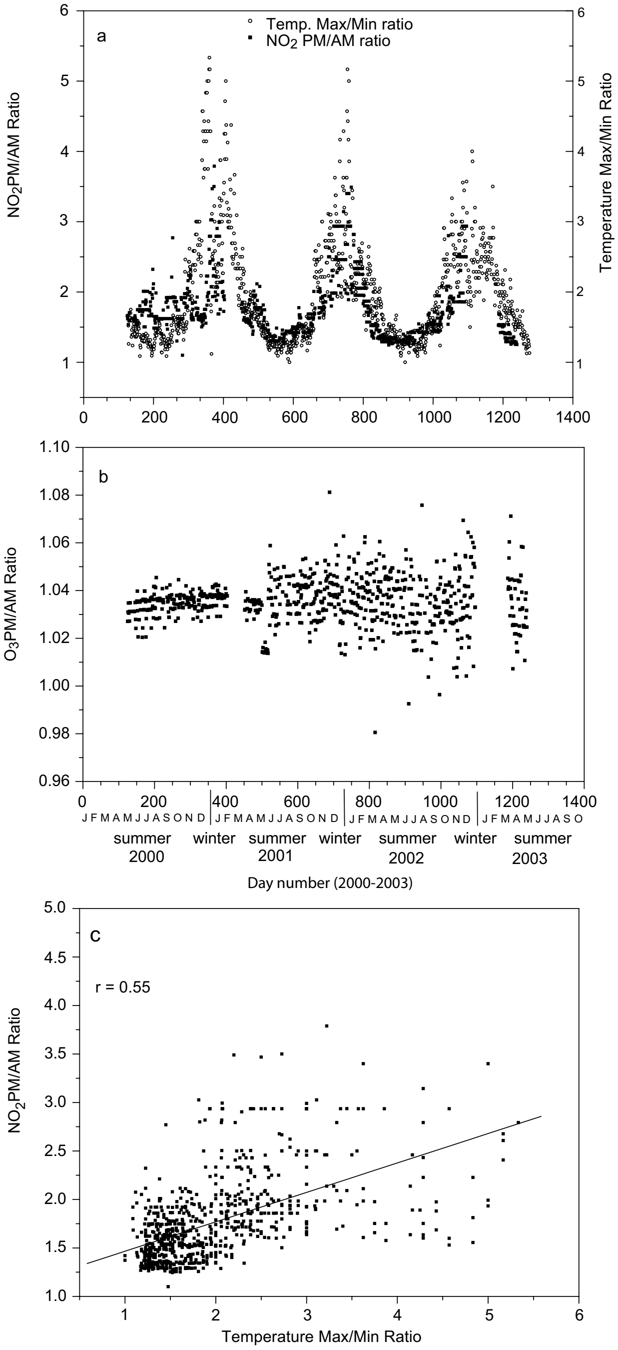

Fig. 5. a) Ratio of NO_2 total column densities of sunset and sunrise and ratio of temperature (max/min) during 2000-2003, b) Same as a) but for O_3, c) Correlation between NO_2 PM/AM ratio and temperature max/min ratio during 2000-2003.

Koike *et al*. (1999) have analyzed the series of PM/AM ratio values of the VCD of NO_2 and found a maximum ratio of 2.32 in winter and a minimum of 1.25 in summer. They obtained residual series of ratio values after eliminating seasonal trends and by considering PM value of the day and AM value of the next day for the two stations: Moshiri (44.4° N, 142.3° E) and Rikubetsu (43.5° N, 143.8° E). A positive correlation between these two stations before and after eliminating seasonal trend is suggestive of day-to-day variation of PM/AM ratios in the VCD of NO_2 in association with the real change in the atmosphere. Otten *et al*. (1998) observed a PM/AM ratio of the VCD of NO_2 of highest value 4.0 during the mid-winter of 1994/1995 at Kiruna (67.9° N, 21.1° E). The analysis at Pune also shows large day-to-day variability in the VCD of NO_2 with maximum PM/AM ratio of about 3.8 in winter compared to small day-to-day variations in spring and summer with PM/AM ratio of about 1.25. However, tropospheric NO_2 pollution probably by local traffic during the day could also enhance the PM/AM ratio in total atmospheric NO_2, in particular during winter when the stratospheric NO_2 is low, and the near surface inversion prevents an efficient dispersion of polluted air (Fiedler *et al*., 1993). During the night NO_2 can be oxidized by O_3 to form NO_3, a strong atmospheric oxidant and a precursor to the formation of N_2O_5. During the day N_2O_5 can be photolyzed to regenerate NO_2 (Nichol *et al*., 1996). In contrast, N_2O_5 can have morning concentrations in the lower stratosphere comparable to NO_x, even though its production requires the formation of NO_3.

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3 + h\nu \rightarrow NO + O_2$

$\rightarrow NO_2 + O$

$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$

In the winter, nights are longest; therefore, during night NO_2 to N_2O_5 conversion is more and hence in the morning NO_2 value will be less, what leads to high PM/AM ratio. During daytime, photochemical reactions take place in the presence of sunlight and N_2O_5 that, formed due to oxidation of NO_2 during night, gets photolyzed to reproduce NO_2 (Kostadinov *et al*., 1999). The formation of NO_2 during the day leads to an increase in the VCD of NO_2:

$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$

The increase in NO_2 VCD is also possible due to increased pollution during day, which reflects in the evening hours as it is seen from figures. At twilight, NO_2 density depends on NO and controlled by the following reactions:

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + h\nu \rightarrow NO + O$

$NO_2 + O \rightarrow NO + O_2$

During evening twilight hours, the rapid decreases in the rate of photolysis of NO_2 and the abundances of atomic oxygen lead to conversion of NO into NO_2. Thus, the total number of NO_2 molecules can increase substantially at evening hours and hence the AM/PM differences (Solomon *et al*., 1987; Kerr *et al*., 1977; Boughner *et al*., 1980). These AM/PM differences in VCD of NO_2 can also be seen in Figure 3a. The VCD data at Pune show strong seasonal and diurnal variations of NO_2, with maxima in summer at sunset and minima in winter at sunrise. This agrees with the results of earlier authors (Noxon *et al*., 1979; Syed *et al*., 1981; Johnston *et al*., 1989; Solomon *et al*., 1992; Bhonde *et al*., 1992; Lal *et al.*, 1993; Kondo *et al*., 1994). From Figure 5b, O_3 PM/AM ratio is slightly higher in winter months compared to summer months. The average PM/AM ratio of about 1.03 is observed. Various nitrogen oxides like NO, NO_2 and NO_3 are involved in reactions, which affect O_3 abundance, N_2O_5 acts as a temporary reservoir for these nitrogen oxides species. Therefore, the concentration of N_2O_5 in the atmosphere contributes to the AM/PM O_3 abundance. However, there is not much difference seen in O_3 values. Hence, no much variation is seen in PM/AM ratio.

5. Conclusions

- Full day observations have been made from morning (SZA 90°) to evening (SZA 90°) to see the diurnal variations of trace gases such as O_3, NO_2, H_2O and O_4. SCD_{diff} of above gases increase smoothly as the AMF increases with SZA. It is seen that evening NO_2 SCD_{diff} are higher compared to morning SCD_{diff}. It is also noticed that evening NO_2 values are almost double of morning NO_2 values in the month of October 2000. These high values of NO_2 in the evening appear to be related to NO-NO_2 conversion that occurs in twilight period. In O_3, H_2O and O_4, no much differences are observed in morning and evening SCD_{diff}.
- A time series of daily VCD of NO_2 and O_3 at sunrise and sunset has been obtained during the period from May 2000 to May 2003. There have been found a good correlation between NO_2 and O_3 VCD during the period. The VCD data at Pune show strong seasonal and diurnal variations of NO_2 with maxima in summer at sunset and minima in winter at sunrise. Ozone has strong seasonal variations but weak diurnal variations at sunrise and sunset hours with maxima in summer and minima in winter. A good agreement is found between O_3 VCD and minimum temperature variations during the above period. High summer ozone values are confined to increased duration of UV-radiation during summer months.
- The percentage difference between VCD obtained from Dobson and our spectrometer varies from 0.8 to 4%. Similarly, in VCD obtained from our spectrometer and TOMS, the percentage difference varies from 1 to 8% during the above period.
- The NO_2 PM/AM ratios are found to be higher in winter months and lower in summer months. It has also been found that temperature max/min ratios are higher in winter and lower in summer months during 2000-2003. When the max/min temperature differences are more, NO_2 PM/AM differences are also observed more. In winter months NO_2 PM/AM ratio goes up to 3.8 and in summer months lowest ratio is 1.25. A positive correlation is found between NO_2 PM/AM ratio and temperature max/min ratio during the period 2000-2003.
- Temperature of the atmosphere controls the rate of the thermal decomposition of N_2O_5 concentrations. N_2O_5 forms during dark hours. In the winter, nights are longest; therefore,

during night NO_2 to N_2O_5 conversion is more and hence in the morning NO_2 value will be less that leads to high PM/AM ratio. Further, during evening twilight hours, the rapid decreases in the rate of photolysis of NO_2 and the abundances of atomic oxygen lead to conversion of NO into NO_2. Thus, the total number of NO_2 molecules can increase substantially at evening hours, and hence the AM/PM differences. O_3 PM/AM ratio is found slightly higher in winter months compared to summer months.

Acknowledgements

The authors are thankful to Prof. B. N. Goswami Director IITM and Dr. P. C. S. Devara Head PM & A Division for his encouragement. The authors are thankful to the Department of Science and Technology (DST), New Delhi, Govt. of India for the financial support during the tenure of this work.

References

Bhonde S. D., P. Mehra, S. Bose, A. L. Londhe and D. B. Jadhav, 1992. Simultaneous measurement of low latitude NO_2 and O_3 from zenith sky observations in visible region. *Indian J. Radio Space Phys.* **21**, 18-25.

Bhosale C. S., G. S. Meena, A. L. Londhe, D. B. Jadhav, O. Puentedara and M. Gil, 2004. Variations of O_3, NO_2 and O_4 densities in association with NAO indices during winter/spring of 1993/94 and 1994/95 at sub-Arctic station. *Indian J. Radio Space Phys.* **33**, 104-114.

Boughner R., J. C. Larsen and M. Natarajan, 1980. The influence of NO and ClO variations at twilight on the interpretation of solar occultation measurements. *Geophys. Res. Lett.* **7**, 231-234.

Bradshaw J., D. Davis, G. Grodzinsky, S. Smyth, R. Newell, S. Sandholm and S. Liu, 2000. Observed distributions of nitrogen oxides in the remote free troposphere from the NASA global tropospheric experiment programs. *Rev. Geophys*. **38**, 61-116.

Erle F., K. Pfeilsticker and U. Platt, 1995. On the influence of tropospheric clouds on zenith-scattered-light measurements of stratospheric species. *Geophys. Res. Lett*. **22**, 2725-2728.

Fiedler M., H. Frank, T. Gomer, M. Hausmann, K. Pfeilsticker and U. Platt, 1993. The 'minihole' event on 6 Feb. 1990: Influence of Mie-scattering on the evaluation of spectroscopic measurements. *Geophys. Res. Lett*. **20**, 959-962.

Gil M., O. Puentedara, M. Yela, C. Parrondo and D. B. Jadhav, 1996. OClO, NO_2 and O_3 total column observations over Iceland during the winter 1993/94. *Geophys. Res. Lett.* **23**, 3337-3340.

Hood L. L., J. P. McCormack and K. Labitzke, 1997. An investigation of dynamical contributions to midlatitude ozone trends in winter. *J. Geophys. Res*. **102**, 13079-13093.

Hudson R. D., J.-H. Kim and A. M. Thompson, 1995. On the derivation of tropospheric column from radiances measured by the total ozone mapping spectrometer. *J. Geophys. Res*. **100**, 11137–11145.

Jadhav D. B., A. L. Londhe, G. S. Meena, D. Jhurry and J. M. Rossett, 1999. Installation of an automatic spectrometer at Mauritius and preliminary result of NO_2 over Mauritius. *Curr. Sci*. **76**, 998-1000.

Jadhav D. B., 2002. Monitoring of atmospheric constituents using UV-visible spectroscopy, Proceedings of National Workshop on Atmospheric Chemistry *(NWAC-99)*, (Devara, P.C.S. and Raj, P.E. Eds.), Indian Institute of Tropical Meteorology, Pune, 145-149 pp.

Jayaraman A. and B. H. Subbaraya, 1988. Vertical distribution of water vapour over Hydarabad. *Indian J. Radio Space Phys*. **17**, 63-68.

Johnston P. V. and R. L. McKenzie, 1989. NO_2 observations at 45° S during the decreasing phase of solar cycle 21, from 1980 to 1987. *J. Geophys. Res*. **94**, 3473-3486.

Kerr J. B., W. F. J. Evans and J. C. McConnell, 1977. The effect of NO_2 changes at twilight on tangent ray NO_2 measurements. *Geophys. Res. Lett*. **4**, 577-579.

Klenk K. F., P. K. Bhartia, A. J. Fleig, V. G. Kaveeshwar, R. D. McPeters and P. M. Smith, 1982. Total ozone determination from the backscattered ultraviolet (BUV) experiment. *J. Appl. Meteor.* **21**, 1672–1684.

Koike M., Y. Kondo, W.A. Matthews, P. V. Johnston, H. Nakajima, A. Kawaguchi, H. Nakane, I. Murata, A. Budiyono, M. Kanada and N. Toriyama, 1999. Assessment of the uncertainties in the NO_2 and O_3 measurements by visible spectrometers. *J. Atmos. Chem*. **32**, 121-145.

Kondo Y., W. A. Matthews, S. Solomon, M. Koike, M. Hayashi, K. Yamazaki, H. Nakajima and K. Tsukuui, 1994. Ground based measurements of column amounts of NO_2 over Syowa Station, Antarctica. *J. Geophys. Res*. **99**, 14535-14548.

Kostadinov I., G. Giovanelli, F. Ravegnani, D. Bortoli and A. Petritili, 1999. Depolarization ratio of the zenith scattered radiation and measured NO_2 slant columns. *Proc. Society of Photo-Optical Instrumentation Engineers* (SPIE), 3754, 402-410.

Kreher K., M. Fiedler, T. Gomer, J. Stutz and U. Platt, 1995. The latitudinal distribution (50° N - 50° S) of NO_2 and O_3 in October/November 1990. *Geophys. Res. Lett*. **22**, 1217-1220.

Lal M., D. K. Chakrabarty, J. S. Sidhu, S. R. Das and S. D. Verma, 1993. Some results of ground-based measurements of atmospheric NO_2 at Ahmedabad by visible absorption spectroscopy. *Indian J. Radio Space Phys*. **22**, 108-113.

Londhe A. L., C. S. Bhosale, G. S. Meena, D. B. Jadhav, M. Gil, O. Puentedara and M. Yela 1999. Vertical profile variations of NO_2 and O_3 using slant column density observations during twilight period. *Indian J. Radio & Space Phys*. **28**, 291-301.

McKenzie R. L. and P. V. Johnston, 1982. Seasonal variations in stratospheric NO_2 of 45° SW. *Geophys. Res. Lett*. **9**, 1255-1258.

Meena G. S., D. B. Jadhav and C. S. Bhosale, 2003. Total column density variations of NO_2 and O_3 by automatic visible spectrometry over Pune, India. *Curr. Sci.* **85**, 171-179.

Meena G. S., C. S. Bhosale and D. B. Jadhav, 2004. Influence of tropospheric clouds on ground-based measurements of stratospheric trace gases at tropical station, Pune. *Atmos. Environ*. **38**, 3459-3468.

Nichol S. E., J. G. Keys, S. W. Wood, P. V. Johnston and G. E. Bodeker, 1996. Intercomparison of total ozone data from a Dobson spectrophotometer, TOMS, visible wavelength spectrometer, and ozonesondes. *Geophys. Rev. Lett*. **23**, 1087-1090.

Noxon J. F., 1975. Nitrogen dioxide in the stratosphere and troposphere measured by ground-based absorption spectroscopy. *Science* **189**, 547-549.

Noxon J. F., E. C. Whipple and R. S. Hyde, 1979. Stratospheric NO_2. 1. Observational method and behavior at midlatitudes. *J. Geophys. Res*. **84**, 5047-5065.

Otten C., F. Ferlemann, U. Platt, T. Wagner and K. Pfeilsticker, 1998. Groundbased DOAS UV/ visible measurements at Kiruna (Sweden) during SESAME winters 1993/94 and 1994/95. *J. Atmos. Chem*. **30**, 141-162.

Pfeilsticker K., F. Erle and U. Platt, 1997. Absorption of solar radiation by atmospheric O_4. *J. Atm. Sci*. **54**, 933-939.

Platt U., 1994. Differential optical absorption spectroscopy (DOAS). In: *Air monitoring by spectroscopic techniques* (M. W. Sigrist, Ed.), John Wiley, New York, Chem. Anal. Ser., 27-84.

Pommereau J. P. and F. Goutail, 1988. O_3 and NO_2 ground-based measurements by visible spectrometry during arctic winter and spring 1988. *Geophys. Res. Lett*. **15**, 891-894.

Senne T., J. Stutz and U. Platt, 1996. Measurements of the latitudinal distribution of NO_2 column density and layer height in Oct./Nov. 1993. *Geophys. Res. Lett*. **23**, 805-808.

Solomon S., A. L. Shmeltekopf and R. W. Sanders, 1987. On the interpretation of zenith sky absorption measurement. *J. Geophys. Res*. **92**, 8311-8319.

Solomon S. and J. G. Keys, 1992. Seasonal variation in Antarctic NO_x chemistry. *J. Geophys. Res*. **97**, 7971-7978.

Solomon S., R. W. Portmann, R. W. Sanders and J. S. Daniel, 1998. Absorption of solar radiation by water vapor, oxygen and related collision pairs in the Earth's atmosphere. *J. Geophys. Res*. **103**, 3847-3858.

Syed M. Q. and A. W. Harrison, 1981. Seasonal trend of stratospheric NO_2 over Calgary, *Can. J. Phys*. **59**, 1278-1279.

Wayne R. P., (Ed), 1991. The nitrate radical: physics, chemistry, and the atmosphere, *Atmos. Environ*. **25**, 1-203.

WMO 1990a. Report of the International Ozone Trends Panel: 1988, Report No. 18, two volumes, WMO, Geneva.