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Study of diurnal and seasonal variation of atmospheric NO2, O3, H2O and O4 at Pune, India
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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 NO₂, O₃, H₂O and O₄. For the study of seasonal behavior of NO₂ and O₃, vertical column densities (VCD) were retrieved during the above period. For the whole period, NO₂ and O₃ 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 NO₂ and O₃ VCD are found in summer months and lowest in winter 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O 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\textsubscript{2} and O\textsubscript{3} are discussed. The evening to morning (PM/AM) ratios of NO\textsubscript{2} and O\textsubscript{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\textsubscript{3} and NO\textsubscript{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\textsubscript{2}, O\textsubscript{3}, H\textsubscript{2}O and O\textsubscript{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\textsubscript{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):

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

(1)

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

$$VCD(\theta) = \frac{(SCD_{\text{diff}}(\theta) + RCD)}{AMF(\theta)}$$

(2)

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

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:

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

or

$$VCD = \frac{SCD_{\text{diff}}(\theta)}{[AMF(\theta) - AMF(\theta_0)]}$$

(3)

where \( \theta_0 \) is the SZA of reference spectrum. For the study of seasonal variations O\textsubscript{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$_2$O 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$_2$O 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$_2$O 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$_2$O 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 water 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$_{diff}$
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Fig. 1. a) Differential slant column densities of NO₂ with solar zenith angles, b) Same as a) but for O₃, c) Same as a) but for H₂O, d) Same as c) but for O₄.

of NO₂, O₃, H₂O and O₄ at morning (AM) and evening (PM) 90° SZA for selected days. From Table I, it is seen that the evening NO₂ values are almost double of morning NO₂ values at 90° SZA. The percentage difference between evening and morning NO₂ SCDdiff values varies from 78 to 107% at 90° SZA during those days. These higher values of NO₂ in the evening particularly at SZA greater than 85° compared to morning NO₂ may have occurred due to increased rate of NO-NO₂ conversion and decreases in the rate of photolysis of NO₂ during evening twilight period. From Table I, it has been seen that evening densities of O₃ are 1-5% higher than morning densities at 90° SZA during those days. H₂O SCDdiff at evening 90° SZA are found to be 2-11% higher than morning SCDdiff of same SZA. Similarly, O₄ SCDdiff are 0-26% higher than morning SCDdiff at evening 90° SZA. On October 19, O₄ SCDdiff at evening is 26% higher than morning. It is also seen that on this day H₂O SCDdiff at evening 90° SZA is 11% higher than morning compared to other days. These higher values of O₄ and H₂O 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 H₂O and O₄, which are good indicative of the increased absorption path lengths due to multiple Mie-scattering inside clouds.
Table I. Differential slant column densities (SCDdiff) of NO2, O3, H2O and O4 at morning (AM) and evening (PM) 90° SZA.

<table>
<thead>
<tr>
<th>Day of October 2000</th>
<th>18</th>
<th>19</th>
<th>21</th>
<th>22</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCDdiff at 90° SZA</td>
<td>NO2</td>
<td>O3</td>
<td>H2O</td>
<td>O4</td>
<td></td>
</tr>
<tr>
<td>(molecules cm$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AM</td>
<td>4.00 × 10$^{16}$</td>
<td>1.11 × 10$^{20}$</td>
<td>1.49 × 10$^{24}$</td>
<td>1.36 × 10$^{44}$</td>
<td></td>
</tr>
<tr>
<td>PM</td>
<td>7.73 × 10$^{16}$</td>
<td>1.15 × 10$^{20}$</td>
<td>1.62 × 10$^{24}$</td>
<td>1.36 × 10$^{44}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.93 × 10$^{16}$</td>
<td>1.13 × 10$^{20}$</td>
<td>1.32 × 10$^{24}$</td>
<td>1.40 × 10$^{44}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.96 × 10$^{16}$</td>
<td>1.15 × 10$^{20}$</td>
<td>1.43 × 10$^{24}$</td>
<td>1.25 × 10$^{44}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.82 × 10$^{16}$</td>
<td>1.16 × 10$^{20}$</td>
<td>1.46 × 10$^{24}$</td>
<td>1.02 × 10$^{44}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.68 × 10$^{16}$</td>
<td>1.17 × 10$^{20}$</td>
<td>1.73 × 10$^{24}$</td>
<td>1.14 × 10$^{44}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2 shows the plots of SCDdiff vs AMF (Langley plot) of O3 at evening on October 18, 19, 21 and 22. The correlation coefficients (r) between SCDdiff 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 O3 and NO2 is given by the random error from the fit. The random error is 1% for O3 and 2% for NO2. Uncertainty in cross sections is 1.2% for O3 and 2.3% for NO2. Pseudo-random error causing structure in the “filling-in” of absorption features by Raman scattered light is 1% for O3 and 5% for NO2. Another factor is that associated with the calculated AMF due to approximations in the RT model, which is 2.7% for O3 and 5% for NO2. The root-sum-square error calculated from these various error sources is approximately 3% for O3 and 8% for NO2.

4.2 Seasonal variation

Figures 3a and b show the daily VCD of NO2 and O3, 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 NO2 and 18.3 for O3, 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 NO2 VCD are found in summer months (May and June) and minimum in winter months (December and January) for all the years.
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Fig. 2. Langley plots (SCD\(_{\text{diff}}\) 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).

<table>
<thead>
<tr>
<th>Day No.</th>
<th>Day of the year 2000</th>
<th>Evening SCD(_{\text{diff}}) at 90° SZA (molec. cm(^{-2}))</th>
<th>Y intercept of Langley plots = RCD 30° (molec. cm(^{-2}))</th>
<th>Slope of Langley plots = VCD (molec. cm(^{-2}))</th>
<th>VCD 90° using eq. (2) (molec. cm(^{-2}))</th>
<th>V(_{\text{Dob}}) (DU)</th>
<th>V(_{\text{TOMS}}) (DU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>292</td>
<td>18 Oct</td>
<td>1.15 \times 10^{38}</td>
<td>7.70 \times 10^{18}</td>
<td>6.67 \times 10^{18}</td>
<td>6.69 \times 10^{18} (249 DU)</td>
<td>259</td>
<td>271</td>
</tr>
<tr>
<td>293</td>
<td>19 Oct</td>
<td>1.15 \times 10^{38}</td>
<td>7.72 \times 10^{18}</td>
<td>6.73 \times 10^{18}</td>
<td>6.71 \times 10^{18} (250 DU)</td>
<td>256</td>
<td>261</td>
</tr>
<tr>
<td>295</td>
<td>21 Oct</td>
<td>1.16 \times 10^{38}</td>
<td>7.79 \times 10^{18}</td>
<td>6.73 \times 10^{18}</td>
<td>6.77 \times 10^{18} (252 DU)</td>
<td>254</td>
<td>258</td>
</tr>
<tr>
<td>296</td>
<td>22 Oct</td>
<td>1.17 \times 10^{38}</td>
<td>7.85 \times 10^{18}</td>
<td>6.80 \times 10^{18}</td>
<td>6.83 \times 10^{18} (254 DU)</td>
<td>256</td>
<td>273</td>
</tr>
<tr>
<td>297</td>
<td>23 Oct</td>
<td>1.18 \times 10^{38}</td>
<td>7.91 \times 10^{18}</td>
<td>6.82 \times 10^{18}</td>
<td>6.88 \times 10^{18} (256 DU)</td>
<td>258</td>
<td>272</td>
</tr>
</tbody>
</table>

V\(_{\text{Dob}}\) and V\(_{\text{TOMS}}\) are ozone vertical column collected from Dobson and TOMS instrument, respectively. January 1, 2000 is considered as day number 1, 1 DU = 2.69 \times 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$_x$ 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
Diurnal and seasonal variation of atmospheric NO$_2$, O$_3$, H$_2$O and O$_4$ 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.

<table>
<thead>
<tr>
<th>Years</th>
<th>Maximum NO$_2$ VCD in molecules cm$^{-2}$ (average of May and June)</th>
<th>Minimum NO$_2$ VCD in molecules cm$^{-2}$ (average of December and January)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Morning</td>
<td>Evening</td>
</tr>
<tr>
<td>2000</td>
<td>5.6 × 10$^{15}$</td>
<td>8.0 × 10$^{15}$</td>
</tr>
<tr>
<td>2001</td>
<td>6.0 × 10$^{15}$</td>
<td>8.1 × 10$^{15}$</td>
</tr>
<tr>
<td>2002</td>
<td>6.5 × 10$^{15}$</td>
<td>8.5 × 10$^{15}$</td>
</tr>
<tr>
<td>2003</td>
<td>7.0 × 10$^{15}$</td>
<td>9.0 × 10$^{15}$</td>
</tr>
</tbody>
</table>

### 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.

<table>
<thead>
<tr>
<th>Years</th>
<th>Maximum O$_3$ VCD in molecules cm$^{-2}$ (average of May and June)</th>
<th>Minimum O$_3$ VCD in molecules cm$^{-2}$ (average of December and January)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Morning</td>
<td>Evening</td>
</tr>
<tr>
<td>2000</td>
<td>7.5 × 10$^{18}$</td>
<td>8.3 × 10$^{18}$</td>
</tr>
<tr>
<td>2001</td>
<td>7.4 × 10$^{18}$</td>
<td>7.6 × 10$^{18}$</td>
</tr>
<tr>
<td>2002</td>
<td>7.3 × 10$^{18}$</td>
<td>7.6 × 10$^{18}$</td>
</tr>
<tr>
<td>2003</td>
<td>7.5 × 10$^{18}$</td>
<td>7.8 × 10$^{18}$</td>
</tr>
</tbody>
</table>

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\textsubscript{2} and O\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} PM/AM ratios are higher in winter months and lower in summer months for all the years. In winter months NO\textsubscript{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\textsubscript{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\textsubscript{2} PM/AM differences are also observed more. The NO\textsubscript{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\textsubscript{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\textsubscript{2}O\textsubscript{5} concentrations. N\textsubscript{2}O\textsubscript{5} forms during the dark hours and is destroyed by photolysis and thermal decomposition. N\textsubscript{2}O\textsubscript{5} concentration is a function of temperature and wavelength. In the winter nights N\textsubscript{2}O\textsubscript{5} forms more
due to more dark hours and in day time it is photolyzed to produce NO₂, which is reflecting in the evening (PM) hours. Hence, in winter PM/AM ratios are higher than in summer.

Fig. 5. a) Ratio of NO₂ total column densities of sunset and sunrise and ratio of temperature (max/min) during 2000-2003, b) Same as a) but for O₃, c) Correlation between NO₂ 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$_2$O$_5$. During the day N$_2$O$_5$ can be photolyzed to regenerate NO$_2$ (Nichol et al., 1996). In contrast, N$_2$O$_5$ can have morning concentrations in the lower stratosphere comparable to NO$_x$, even though its production requires the formation of NO$_3$.

\[
\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_3 + \text{hv} & \rightarrow \text{NO} + \text{O}_2 \\
& \rightarrow \text{NO}_2 + \text{O} \\
\text{NO}_3 + \text{NO}_2 + \text{M} & \leftrightarrow \text{N}_2\text{O}_5 + \text{M}
\end{align*}
\]

In the winter, nights are longest; therefore, during night NO$_2$ to N$_2$O$_5$ 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$_2$O$_5$ 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$_2$.

\[
\text{N}_2\text{O}_5 + \text{hv} \rightarrow \text{NO}_3 + \text{NO}_2
\]

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:

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2
\end{align*}
\]

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\textsubscript{2} can also be seen in Figure 3a. The VCD data at Pune show strong seasonal and diurnal variations of NO\textsubscript{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\textsubscript{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\textsubscript{2}, and NO\textsubscript{3} are involved in reactions, which affect O\textsubscript{3} abundance. N\textsubscript{2}O\textsubscript{5} acts as a temporary reservoir for these nitrogen oxides species. Therefore, the concentration of N\textsubscript{2}O\textsubscript{5} in the atmosphere contributes to the AM/PM O\textsubscript{3} abundance. However, there is not much difference seen in O\textsubscript{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\textsubscript{3}, NO\textsubscript{2}, H\textsubscript{2}O and O\textsubscript{4}. SCD\textsubscript{diff} of above gases increase smoothly as the AMF increases with SZA. It is seen that evening NO\textsubscript{2} SCD\textsubscript{diff} are higher compared to morning SCD\textsubscript{diff}. It is also noticed that evening NO\textsubscript{2} values are almost double of morning NO\textsubscript{2} values in the month of October 2000. These high values of NO\textsubscript{2} in the evening appear to be related to NO-NO\textsubscript{2} conversion that occurs in twilight period. In O\textsubscript{3}, H\textsubscript{2}O and O\textsubscript{4}, no much differences are observed in morning and evening SCD\textsubscript{diff}.

- A time series of daily VCD of NO\textsubscript{2} and O\textsubscript{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\textsubscript{2} and O\textsubscript{3} VCD during the period. The VCD data at Pune show strong seasonal and diurnal variations of NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} PM/AM differences are also observed more. In winter months NO\textsubscript{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\textsubscript{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\textsubscript{2}O\textsubscript{5} concentrations. N\textsubscript{2}O\textsubscript{5} forms during dark hours. In the winter, nights are longest; therefore,
Diurnal and seasonal variation of atmospheric NO$_2$, O$_3$, H$_2$O and O$_4$
during night NO$_2$ to N$_2$O$_5$ 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$_3$. 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.

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