Atmospheric total ozone content from spectral extinction measurements

S K Sathesh, K Krishna Moorthy
(Space Physics Laboratory, Vikram Sarabhai Space Centre, Trivandrum 695 022)
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The estimation of columnar content of atmospheric ozone from multispectral solar extinction measurements in the visible and near infra-red range is described and has been applied to the ground-based multiwavelength solar radiometer (MWR) data for the period December 1993-May 1995 at the coastal station, Trivandrum (8.55°N, 77°E). The estimated values of total ozone content compare well, on an average, with the climatological monthly means obtained from other measurements, except during the monsoon months. The disagreement during monsoon months appears to be the manifestations of local meteorological processes which cause significant changes in the aerosol size distribution and hence the spectral variation of aerosol optical depths.

1 Introduction

Though essentially a trace constituent, the atmospheric ozone plays an important role in the earth's radiation budget. Fairly accurate (≈ 10%) estimates of columnar ozone content are required in many scientific applications including radiation budget of the stratosphere, solar radiometry (for deducing aerosol optical depths) and in calculations involving solar UV-B transmittance. Several methods exist for the determination of the total ozone content of the atmosphere as well as its altitude distribution. Historically, the columnar content of ozone has been determined by measuring the absorption of solar UV radiation by ozone, using photoelectric spectrophotometers1,2. In situ measurements using balloons and rockets2,3 have yielded its altitude distribution. Using broad band sun photometer measurements Acharya et al.1 deduced the columnar ozone content, while Subbaraya et al.3 used a Brewer spectrophotometer to estimate the columnar ozone content at Trivandrum and to study its diurnal variations. Total ozone mapping spectrometers (TOMS) provide a global coverage of total ozone from space-borne measurements. Multispectral solar extinction measurements, in the visible and near infra-red range, using ground-based multiwavelength radiometers (MWR) have also been used to estimate atmospheric columnar ozone content5,6. This method, though has limited application, is convenient and would provide fairly accurate estimates (within about 10%) of the total ozone content when the aerosol features remain rather steady without being significantly influenced by regional scale processes. Thus, this method can be applied at remote locations where more accurate measurements are not available and when highly accurate estimates of total ozone are not required. In this paper, the principle of the method is outlined and has been applied to deduce average total ozone content at the coastal station, Trivandrum (8.55°N, 77°E). The results are compared with other measurements.

The principle of estimating total ozone content from spectral extinction measurements is very similar to the conventional differential absorption technique, applied to two closely spaced wavelengths in the UV region where it is assumed that the aerosol optical depth is wavelength independent between these two wavelengths. The spectral extinction method, however, makes use of measurements made on the Chappius band of ozone. Though a weak band by itself, it is quite useful in estimating total O3 from solar spectral extinction measurements. The Chappius band is a near continuum and broad, extending from ≈ 450 nm to ≈ 750 nm with a peak at ≈ 600 nm, so that the wavelength variation of aerosol optical depth has to be properly accounted for, while retrieving ozone.

2 Outline of the method

Using a ground-based MWR, atmospheric columnar total optical depths, \( \tau_\lambda \) are determined at a number of narrow wavelength bands centred at \( \lambda \), following the conventional Langley plot method of evolving a least square fit to the Beer-Lambert law7,8. The set of wavelengths (\( \lambda \)) is so selected
that some of them lie within the Chappius band (at least one around its peak) and some lie on either side of the band. Care is also taken so that the wavelengths do not fall in the absorption bands of any other molecular species. In such case

\[ \tau_s = \tau_R(\lambda) + \tau_p(\lambda) + x a(\lambda) \] ... (1)

where, \( \tau_R(\lambda) \) is the optical depth due to Rayleigh scattering, \( \tau_p(\lambda) \) that due to aerosol extinction, \( x \) the columnar ozone content (which is the unknown) and \( a(\lambda) \) the wavelength-dependent absorption cross-section of ozone for the Chappius band. By subtracting \( \tau_R(\lambda) \) from \( \tau_s \) relevant to each \( \lambda \) for the location, we get a reduced optical depth \( \tau_p(\lambda) \), which is a function of \( \tau_p(\lambda) \) and the total ozone content \( x \), so that

\[ \tau_p(\lambda, x) = \tau_p(\lambda) + x a(\lambda) \] ... (2)

The wavelength variation of aerosol optical depth in the range of \( \lambda \) can be expressed by the simple Angström formula written in logarithmic form as

\[ \log \tau_p(\lambda) = \log \beta - \alpha \log(\lambda) \] ... (3)

where, \( \beta \) is the turbidity parameter and \( \alpha \) the wavelength exponent. However, this formula is applicable when the aerosol size distribution (columnar) follows a Junge power-law distribution. Recent experimental evidences\(^9,10\) indicate that in many practical cases the aerosol columnar size distribution (CSD) deviate from a simple inverse power-law form. This will lead to curvature in \( \tau_p - \lambda \) variation (in a log-log scale) which, otherwise, would follow a straight line with slope \( v = \alpha + 3 \). To account for any such curvature, a second order term is added to Eq. (3) following King and Byrne\(^5\), so that

\[ \log \tau_p(\lambda) = a_0 + a_1 \log \lambda + a_2 (\log \lambda)^2 \] ... (4)

where, \( a_0 = \log \beta \), \( a_1 = -\alpha \) and \( a_2 \) are regression coefficients.

From Eq. (2), we have

\[ \tau_p(\lambda, x) = \tau_p(\lambda) - x a(\lambda) \] ... (5)

In Eq. (5), \( \tau_p(\lambda) \) are the values estimated from MWR measurements, \( x \) is the total ozone content (which is unknown) and \( a(\lambda) \) is known for various values of \( \lambda \). Denoting \( \tau_p(\lambda, x) \) by \( \tau^*_p(\lambda) \) to represent the values deduced from MWR measurements, Eq. (5) can be written as

\[ \log \tau^*_p(\lambda, x) = \log \{ \tau_p(\lambda) - x a(\lambda) \} \] ... (6)

The technique of estimating total ozone involves estimation of \( \log \tau^*_p(\lambda) \) using Eq. (6) by varying \( x \) from zero and evolving a best fit with Eq. (4).

The value of \( x \) for which the fit yields the lowest r.m.s. error is taken as the optimum value of the ozone content. The goodness of fit is quantitatively established by minimizing \( x^2 \) which is defined as

\[ x^2 = \sum \frac{1}{\sigma_i^2} [\log \tau^*_p(\lambda_i, x) - (a_0 + a_1 \log \lambda_i + a_2 (\log \lambda_i)^2)]^2 \] ... (7)

where, \( \sigma_i \) is the standard deviation of \( \log \tau^*_p(\lambda_i) \) obtained as the propagated value of the standard deviation \( \sigma(\lambda_i) \) of \( \tau^*_p(\lambda_i) \) (measurements) and is evaluated using theory of propagation of errors\(^11\) which is given as

\[ \sigma_i^2 = \sigma^2 \left[ \frac{\delta \log \tau^*_p}{\delta \tau^*_p} \right]^2 \]

\[ = \sigma^2 \left[ \frac{\log e}{\tau^*_p(\lambda_i) - x a(\lambda_i)} \right]^2 \] ... (8)

In Eqs (3)-(8) all the logarithms are to the base ten. The coefficients \( a_0, a_1 \) and \( a_2 \) are evaluated by equating to zero the partial derivatives of \( x^2 \) w.r.t. \( a_0, a_1 \) and \( a_2 \) and solving the resulting set of simultaneous equations. In actual practice \( a(\lambda) \) values as a function of \( \lambda \) are taken from the ozone absorption data\(^12\) and \( x \) is varied from zero in steps; each time \( a_0, a_1 \) and \( a_2 \) are evaluated and \( x^2 \) is estimated using Eq. (7). Initially when \( x \) is small, \( x^2 \) will be large and the iteration on \( x \) is done by giving large increments to \( x \). As \( x^2 \) becomes lower and lower, the increments on \( x \) are made smaller and smaller till the minimum is attained. Reducing the increments on \( x \), as one approaches the minimum in \( x^2 \), helps to identify the optimum value of \( x \) accurately at which \( x^2 \) is minimum. Further, increase in \( x \) leads to increase in \( x^2 \) value. In order to locate the minimum quantitatively, the parameter \( (dx^2/dx) \) is evaluated each time and the value of \( x \) for which \( dx^2/dx = 0 \), is taken as the optimal value.

3 Experimental data

The experimental data used for this study have been obtained using an MWR operating at Trivandrum since December 1993. This system is essentially similar to the one described earlier\(^7,13\), but has been re-designed to facilitate automatic operation using an improved optics unit on an equatorial mount and PC-based control and data acquisition system which enables data collection at desired intervals using an interactive menu. A 12-bit sampling ADC is used to get an improved res-
olution (1/4096). Using this system, atmospheric columnar total optical depth, $\tau_\lambda$, are obtained following conventional Langley technique on clear days at wavelengths centered at 400, 450, 500, 600, 650, 750, 850, 935 and 1025 nm (having full width half maximum bandwidth between 5 and 10 nm). From $\tau_\lambda$ thus obtained, the contribution, $\tau_(O_3)(\lambda)$, due to Rayleigh scattering is subtracted to get the reduced optical depth $\tau_(O_3)(\lambda)$ [the $\tau_(O_3)(\lambda)$ value is estimated using the neutral atmosphere reference model for Trivandrum and the wavelength dependent Rayleigh scattering cross-sections as described by Moorthy et al.13] which is the sum of aerosol optical depth $\tau(a)(\lambda)$ and the optical depth, $\tau_(O_3)(\lambda)$, due to absorption by $O_3$. Water vapour has a strong absorption band at $\sim$935 nm and a weak absorption at $\sim$850 nm and as such these wavelengths are not suitable for application of this technique. Of the remaining seven wavelengths, 500, 600 and 650 nm lie well within the Chappius band 450-750 nm near its ends (with peak around 600 nm) and those at 400 and 1025 nm lie well outside it. Thus, $\tau_(O_3)(\lambda)$ values obtained at these seven wavelengths are used to retrieve ozone following the method outlined here.

4 Application of the method

The method, outlined in Sec. 2, has been applied to the above data to retrieve the total ozone content $x$. A typical example for 6 Dec. 1994 is shown in Fig. 1, where the continuous line shows the variation of $\tau_(O_3)(\lambda)$ as a function of $\lambda$ for the seven wavelengths. By varying $x$ from zero, in steps, and using values of $a(\lambda)$ as applicable for various wavelengths12, $x^2$ is estimated as a function of $x$ using Eq. (7). The derivative of $x^2$ w.r.t. $x$ also is estimated in each case. Figure 2 shows the variation of $x^2$ (top panel) and $dx^2/dx$ (bottom panel) as a function of $x$. As pointed out in Sec. 2, as $x^2$ decreases, the increments are made smaller and the minimum value of $x^2$ corresponds to the optimum value of $x$ for which the fit between Eq. (4) and (6) yields minimum r.m.s. error. At this value of $x$, $dx^2/dx$ becomes zero and then increases to positive as $x$ increases further. The optimum value of $x$ for which $dx^2/dx=0$ (i.e. $x^2$ is minimum) is marked by dashed line in Fig. 2. The dotted line in Fig. 1 corresponds to $\tau_(O_3)(\lambda)$ values estimated using Eq. (4) and the regression coefficients $(a_1, a_2, a_3)$ corresponding to this optimum value of $x$, while the dashed line shows the values of $\tau_(O_3)(\lambda)$ estimated from Eq. (5) by using the optimum value $x$ and the MWR estimated value of $\tau_(O_3)(\lambda)$. A very good agreement between the two is clearly seen in Fig. 1. The residual error between the fitted and estimated values is only 0.001. The optimum value of ozone $(x)$ thus estimated is 239.4 Dobson Units (DU) and is written on the top left corner in Fig. 2.

5 Results and discussion

The method outlined in Sec. 2 has been applied to the MWR data obtained at Trivandrum during the period December 1993-May 1995. Only those days in which $\tau_(O_3)(\lambda)$ variations were rather smooth
without any abrupt changes, thereby depicting a stable aerosol characteristics during a day, have been considered. Thus the number of days in a month varied from three to seven, depending on the sky conditions and season. Typical examples for four different days (in January, February, April and May) are shown in Fig. 3. It can be seen that there is a very good agreement between the values of $\tau_p$ obtained from $\tau_a$ (after subtracting optical depth due to ozone absorption for the optimum value of $x$ obtained using this technique) and $\tau_p$ estimated from Eq. (4). The optimum value of ozone content estimated in each case is 265 DU and shown in each block. In all these cases the r.m.s. error has been very small lying in the range 0.001-0.003. The entire $\tau_a(\lambda)$ data have been analysed in a similar manner and the optimum value of $x$ has been estimated in each case. These are then averaged over identical months and the average value ($X_m$) is taken as the representative value for each month. Though this is not strictly valid for the months June-November owing to the scarcity of MWR data arising due to adverse sky conditions, such a representation is taken in order to compare these values with those obtained by other measurements, particularly, because no daily measurements of total ozone are available for Trivandrum. The variations of $X_m$ are shown in Fig. 4 with the vertical bars representing the standard error. In Fig. 4 the total ozone content (over Trivandrum) shows a weak fluctuation about a mean value of $\sim 255$ DU, with a peak in April ($\sim 300$ DU) and a minimum ($\sim 220$ DU) in July. However, studies using long term Dobson spectrophotometer data at a low latitude station Kodaikanal (10°N) have shown that the total ozone has a peak value of $\sim 280$ DU in June and a minimum value $\sim 245$ DU in December-January with an annual mean value of $\sim 262$ DU. The annual mean obtained from MWR (255.6 ± 6 DU) is well in agreement with the above value within the error bars. From Brewer spectrophotometer measurements at Trivandrum, Subbaraya et al. have reported columnar ozone content in the range 265-280 DU for the period March-May 1990, with considerable day-to-day variations. The values for the same months deduced from MWR measurements lie between 253 and 298 (±15) DU. As there are no total ozone measurements available at Trivandrum and as the IMD ozone balloon sonde are limited in the altitude coverage, a one-to-one comparison has not been possible. However, the total ozone content data for Trivandrum for the period 1991-92 obtained from the TOMS measurements are used to obtain the monthly mean values ($X_T$) and

![Figure 3](image-url)
these are compared with those estimated from MWR data (i.e. with $X_M$). In Table 1, $X_T$, $X_M$ and $\Delta X$ are tabulated for each month. Here $\Delta X$, the percentage deviation of $X_M$ from $X_T$ is given by

$$\Delta X = \frac{X_T - X_M}{X_M} \times 100 \quad \ldots \quad (9)$$

The 4th column of Table 1 shows the number of days ($N$) of MWR data that has been used to obtain $X_M$ for a particular month. Table 1 shows that $X_T$ and $X_M$ compare well during January-May and November and December, while during the period June-September $X_M$ is significantly lower than $X_T$. In fact, the variation of $X_T$ are very much similar to those reported by Kundu\textsuperscript{14} from Dobson data, but are higher by $\sim 10$ to 15 DU during May-August.

The method of estimating total ozone content from spectral extinction measurements offers a handy means of inferring total ozone, particularly, at locations devoid of other routine measurements. Such estimates, particularly, the monthly means, are useful in giving ozone content values that can be used for applications where climatological means are required (e.g. to account for ozone absorption in sun photometry). However, the accuracy of the retrieved ozone content is dependent on how accurately Eq. (4) depicts the wavelength dependence of $\tau_0(\lambda)$. It also depends strongly on the absolute value of $\tau_0(\lambda)$ and its relative contribution to $\tau_s(\lambda)$. A detailed account of the accuracy of this method, \textit{vis-à-vis} the UV spectrophotometer techniques, is given by Shaw\textsuperscript{6}. As has been pointed out therein, the absorption coefficient of O$_3$ at the peak of the Chappius band ($\sim 600$ nm) is much smaller (by about a factor of 6) than its value in the UV-B region ($\sim 320$ nm) and, as a result, any significant deviation in the fit between Eqs (4) and (6), arising out of the deviation of the wavelength dependence of $\tau_p(\lambda)$ from the assumed form [Eq. (4)], will strongly influence the retrieved ozone content. This will, particularly, be so when $\tau_p(\lambda)$ as such is much larger than $x a(\lambda)$ so that a major fraction of $\tau_s(\lambda)$ is contributed by $\tau_p(\lambda)$. It has been pointed out\textsuperscript{6} that when the aerosol optical depth is around 0.2 at mid-visible wavelengths (about an order greater than the typical ozone optical depth at the peak of the Chappius band) the ozone content retrieved from spectral extinction measurements can match with those from Dobson measurements only within $\sim 20\%$. This would also be a reason for the significant deviation (Fig. 4 and Table 1) in $X_M$ from $X_T$ or in the climatological values\textsuperscript{14} seen especially during monsoon months of June to September. Using long term optical depth measurements at Trivandrum, Moorthy \textit{et al.}\textsuperscript{7} have shown that the monthly mean values of $\tau_p(\lambda)$ at

<table>
<thead>
<tr>
<th>Month</th>
<th>$X_T$(DU)</th>
<th>$X_M$(DU)</th>
<th>$N$</th>
<th>$\Delta X$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>244.2±4.4</td>
<td>242.5±27.2</td>
<td>10</td>
<td>+0.7</td>
</tr>
<tr>
<td>February</td>
<td>257.9±5.6</td>
<td>248.0±17.6</td>
<td>10</td>
<td>+4.0</td>
</tr>
<tr>
<td>March</td>
<td>272.2±4.6</td>
<td>288.2±18.4</td>
<td>6</td>
<td>-5.6</td>
</tr>
<tr>
<td>April</td>
<td>275.8±4.6</td>
<td>298.0±15.8</td>
<td>7</td>
<td>-7.5</td>
</tr>
<tr>
<td>May</td>
<td>282.7±4.7</td>
<td>252.5±10.9</td>
<td>9</td>
<td>+12.0</td>
</tr>
<tr>
<td>June</td>
<td>290.1±7.0</td>
<td>238.0±10.5</td>
<td>3</td>
<td>+21.9</td>
</tr>
<tr>
<td>July</td>
<td>288.9±6.9</td>
<td>218.5±27.9</td>
<td>3</td>
<td>+32.2</td>
</tr>
<tr>
<td>August</td>
<td>288.4±5.3</td>
<td>223.2±09.9</td>
<td>3</td>
<td>+29.2</td>
</tr>
<tr>
<td>September</td>
<td>278.9±7.2</td>
<td>235.4±20.4</td>
<td>3</td>
<td>+18.5</td>
</tr>
<tr>
<td>October</td>
<td>269.3±8.3</td>
<td>No Data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>November</td>
<td>253.2±6.8</td>
<td>259.5±30.4</td>
<td>2</td>
<td>-2.4</td>
</tr>
<tr>
<td>December</td>
<td>244.4±6.7</td>
<td>256.2±19.0</td>
<td>7</td>
<td>-4.6</td>
</tr>
</tbody>
</table>
Trivandrum generally lies in the range 0.2-0.3 at mid-visible wavelengths. The above aspects have been examined by plotting the variation of the residual r.m.s. deviation (between the measured values and the fitted values) for each month considered for this study and these are shown in Fig. 5. It can readily be seen that the r.m.s. deviation is much higher during June-November compared to other months indicating that the fit is not very good during these months. This would probably be arising out of the significant local source and sink effects associated with monsoon, causing significant changes in aerosol CSDs (and thus on the wavelength variation of aerosol optical depth) at Trivandrum, as has been reported by Moorthy et al.\textsuperscript{9}. The interplay between strong wet removal associated with monsoon rainfall and marine aerosol input caused by strong surface westerlies would lead the aerosol CSD to show significant variation during these months\textsuperscript{4}. As such, Eq. (4) may not be able to depict the variation of $\tau_{p}(\lambda)$ with $\lambda$ in these months as accurately as it does in other months. This fact is corroborated by the high values of the residual r.m.s. deviation seen during these months (Fig. 5). As has been pointed out earlier, any significant deviation in the spectral variation of aerosol optical depth (from the assumed form) would highly influence the total ozone estimates by this method owing to the weak nature of the Chappius band. As such, the estimates during monsoon months would be more erroneous. Moreover, the number of clear days on which MWR observations could be made is much small during these months as can be seen from the value of $N$ in Table 1. Consequently, the monthly mean values ($X_{M}$) would not be typically representative of the period covered by $X_{T}$.

6 Conclusions
Spectral extinction measurements provide a handy means to retrieve total columnar ozone content of the atmosphere where only fairly accurate estimates (within $\pm$ 5%) are required and at locations where more accurate measurements are not available. However, this technique will yield satisfactory results only during periods when the aerosol columnar size distributions are not significantly influenced by regional source and sink effects, leading to significant changes in the wavelength variation of aerosol optical depths.

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References


