

Total column density of ozone at coastal station Devgad (16°24'N, 73°26'E) measured using portable visible spectrometer

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Abstract Ozone measurements are carried out at coastal station Devgad (16°24'N, 73°26'E) by measuring the solar spectral extinction in the Chappuis band. The measurements are carried out during the months December, January, February, March and April from the year 1996 to 1999. The monthly mean total ozone shows a definite increasing trend from the month of December to April. No significant change is observed in the average value of the total ozone calculated for five months during the years 1996 to 1999.

Keywords ozone column, tropical coastal site, ozone variation

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1. Introduction

In both the troposphere and stratosphere, ozone formation and destruction take place mainly through reactive cycles involving primary and secondary photochemical processes, and as such, they depend strongly on ambient earth's solar radiation field with implications to atmospheric chemistry, life processes and the earth's energy balance. Also, ozone can be considered as the backbone for many chemical processes that occur in both the stratosphere and troposphere, in the sense that most atmospheric reactions either depend on this gas directly or at least in conjunction with free radicals that are generated in various ozone-related cycles. Ozone is ubiquitous component of the atmosphere and is essential for the existence of life on the earth. Ozone affects the solar radiation in the earth's atmosphere [1]. In the natural atmosphere, ozone is formed in the stratosphere by photochemical reaction of solar ultraviolet radiation (<242 nm) with oxygen molecules. Ozone also strongly absorbs ultraviolet radiations (220-320 nm) in the Hartley-Huggins bands.

In recent years, the concentration of stratospheric ozone has been observed to decrease markedly over Antarctica every year during September-October [2]. Measurements in higher latitudes also indicate a systematic decrease in the average

ozone amount in the stratosphere and an increase in the troposphere as a green-house gas, exerting a radiative effect much like to CO₂ [3, 4]. Tropospheric concentration of ozone is influenced by the distribution of CH₄, CO, CO₂, NO, NO₂, N₂O and non-methane hydrocarbons. Although tropospheric ozone makes up only about 10 percent of all the total ozone in the atmospheric column, its presence is central to the problem of the oxidizing efficiency of the troposphere. Present evidence indicates that tropospheric ozone is increasing globally, especially in the upper tropospheric regions. Ozone forms a thin shield protecting the biosphere from the biologically harmful solar UV radiation. Due to industrialization and increased human activities, many molecules of anthropogenic origin have been injected into the atmosphere, which contribute to the depletion of stratospheric ozone and cause higher concentration of tropospheric ozone. A systematic decrease in stratospheric ozone amount since 1975 followed by a much more pronounced decrease after 1979 was reported [5]. The total ozone mapping spectrometer (TOMS) satellite observations reported low global total ozone values for the year 1992-93. The largest decrease in the ozone amount being observed in the region from 10°S to 20°S and 10°N to 60°N latitude. TOMS data reported deficiencies in total ozone by about 11 to 13% for the entire season, winter to

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spring, between 45°N to 65°N in three continents, namely, north America, Europe and Siberia, during the two consecutive years 1991-92 to 1993-94 [6]. In the context of reported ozone depletion in the stratosphere and increase of ozone in the troposphere at some parts of the globe, it would be worthwhile to monitor ozone.

2. Observation technique and data collection

Griggs [8], Solomon *et al* [9] and Amoruso *et al* [7] have recognised that O_3 could be measured by taking advantage of its structural absorption near 600.0 nm wavelength [7-9]. These measurements could be made from ground, where this spectral region except absorption band of water vapour and O_4 is almost free from atmospheric structural absorption. Schiff [10] suggested that O_3 measurements are possible in visible region because of large spatial and temporal variability of ozone. Such O_3 observations were carried out by McKenzie *et al* [11] and Solomon *et al*, [9]. Since then, a great deal of information regarding O_3 has been obtained through ground-based solar zenith sky observations [12-17].

Ozone has an absorption spectrum extending from ultraviolet to infrared with strong absorption in the ultraviolet region. The spectrum has also a pronounced structure in the visible region (Chappuis band), especially in the wavelength range 550 nm to 650 nm [18]. Ozone possesses a highly structural absorption spectrum in the visible region and may absorb as much as a few percent of the incoming solar radiation at large zenith angles in the band near 550 to 650 nm. The total column abundance of stratospheric O_3 can therefore be readily observed from the ground through measurement of absorption in the visible region [9, 19].

The spectral region between the wavelengths 550 nm to 650 nm also contains the structural absorption of H_2O and O_4 . There is an absorption band of water vapour ranging from 560 to 610 nm with peak absorption near 590 nm and absorption band of O_4 ranging from 555 to 590 nm with peak absorption near 575 nm. Therefore, we have simultaneously calculated O_3 , H_2O and O_4 slant column densities from the observations of solar spectral intensities and using matrix inversion technique. The absorption cross sections of O_3 were taken from Griggs data [8]. The absorption cross sections of H_2O were taken from Johnson and McKenzie [20] and absorption cross section of O_4 have been taken from Gill's data given in Greenbiatt *et al* [21].

We have estimated O_3 , H_2O and O_4 column densities at Devgad (16°24'N, 73°26'E) a tropical coastal station using solar spectral intensities data and results of O_3 are presented in this paper. A portable visible spectrometer was used for the measurement of solar spectral intensities. The solar spectral intensities were measured on clear sky days for the months January, February, March, April and December from the year 1996 to 1999. The solar spectral intensities are measured for fifteen different wavelengths between 554.0 nm and 620.0 nm spectral range and are measured during evening two hours at

an interval of every five minutes. One observation is recorded at noon time, taken as reference. The evening time zenith sky spectra are preferred for the following reasons.

- During this time, air mass factor changes considerably
- The large optical path through the atmosphere increases the sensitivity of observations.

The ratio of spectra during evening time and noon time gives the ratio spectrum. Fraunhofer absorption, Rayleigh scattering due to atmospheric gases and instrumental functions are eliminated in the ratio spectrum. The ratio spectrum provides the structural absorption features of O_3 , H_2O and O_4 . This also eliminates the necessity of computing the extra terrestrial values of intensities for the wavelengths under consideration.

3. Results and discussion

The total column density of any atmospheric constituent is defined as the number of molecules of the atmospheric constituent in a volume having one square centimeter cross section area and length equal to the length travelled by the solar radiation in the earth's atmosphere when the Sun is at vertical *i.e.* at zero degree zenith angle. The slant column densities of O_3 are obtained using the matrix inversion technique. From the slant column densities of O_3 , the total column densities of O_3 are obtained by dividing the slant column densities by respective air mass factors. Taking into consideration the location, height from the sea level and time of sunrise at the place of observation the solar zenith angles for different time of observations are calculated from the computerized programme. The air mass factors of ozone for the different zenith angles are calculated from Kastens modified formula for the surface level observations [22]. The total column density of O_3 does not

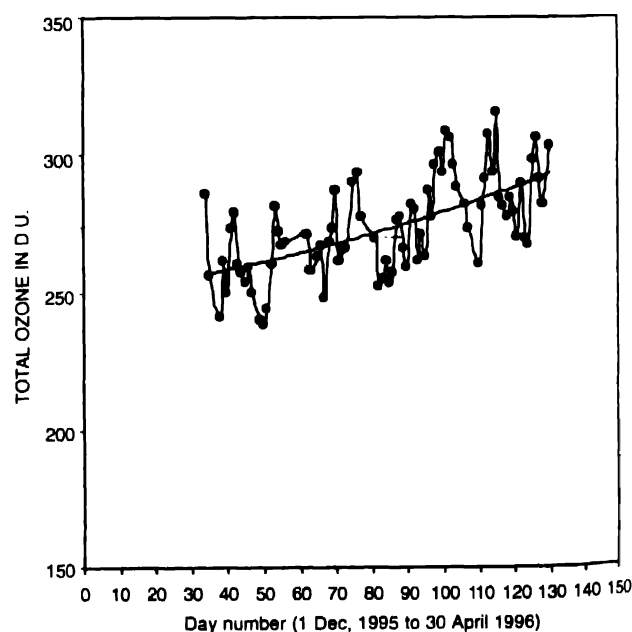


Figure 1. Day-to-day variation for total ozone in the year 1996.

show any definite increasing or decreasing trend within the two hours of observation in the evening.

From the observed total column densities of O_3 for the observations at different times of the day, the mean column density is calculated. This mean value is taken as the total column density of O_3 for that day. The total column density of ozone is also called as total ozone. Total ozone is generally represented in the Dobson Unit (DU) (One DU is equal to 2.687×10^{16} molecules of O_3). The observations are recorded from 1st December to 30th April of the next year and these days are numbered from 1st to 150th. The observed total ozone for the

year 1996 and its day-to-day variation is presented in Figure 1. The day-to-day variations of total ozone for the year 1997, 1998 and 1999 are presented in Figures 2 to 4 respectively. From these day-to-day variation of total ozone, the following important points may be noted.

- (i) Figures 1 to 4 indicate absolute values of total ozone measured at coastal station Devgad ($16^{\circ}24'N, 73^{\circ}26'E$).
- (ii) It is found that there is a change in total ozone from day to day.
- (iii) It is observed that the changes in the day-to-day values of total ozone, for most of the days are about ± 10 DU in the years 1996, 1998 and 1999. However, this change is about ± 20 DU for the year 1997 about the mean value of ozone.
- (iv) For all the four years of observations it is noticed that total ozone show increasing trend from the month of December to April. The above observed trends of variation of total ozone from December to April is in close agreement with those observed at Pune, Kodaikanal and at New Delhi [22-26].
- (v) The absolute values of total ozone measured at coastal station Devgad ($16^{\circ}24'N, 73^{\circ}26'E$) are in close agreement with those at Kodaikanal ($10^{\circ}6'N, 77^{\circ}17'E$). However, these are slightly less than at Pune ($18^{\circ}17'N, 73^{\circ}32'E$). This is confirmed by taking the monthly mean ozone data at Pune [23-28].

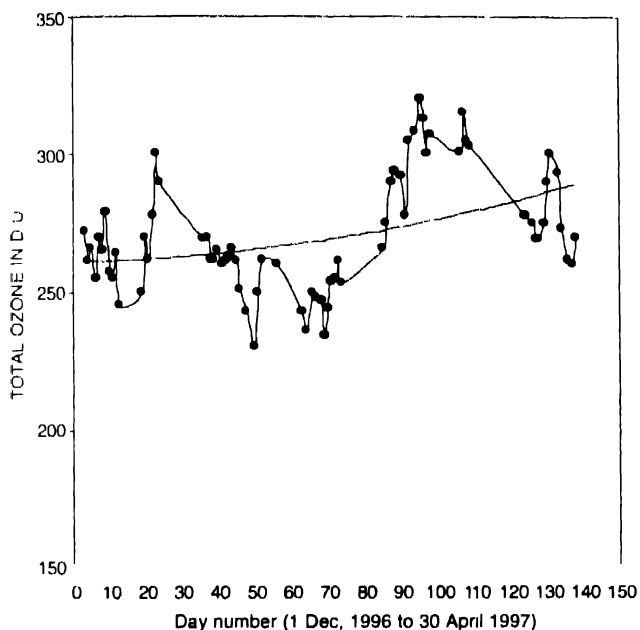


Figure 2. Day-to-day variation for total ozone in the year 1997

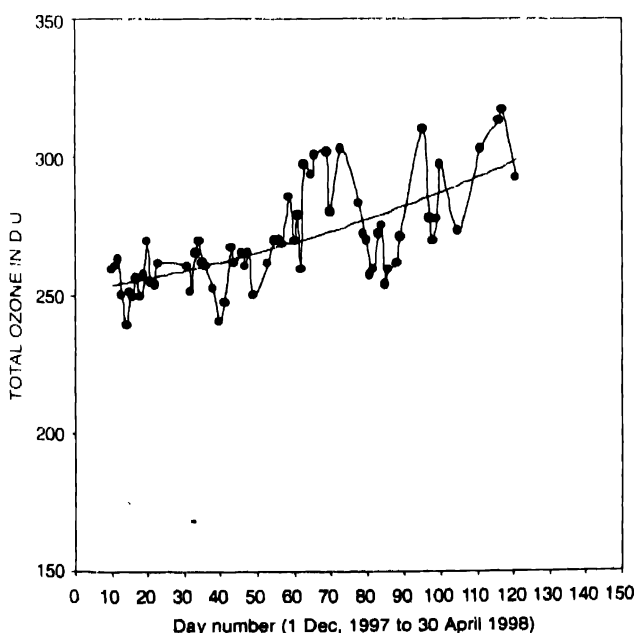


Figure 3. Day-to-day variation for total ozone in the year 1998.

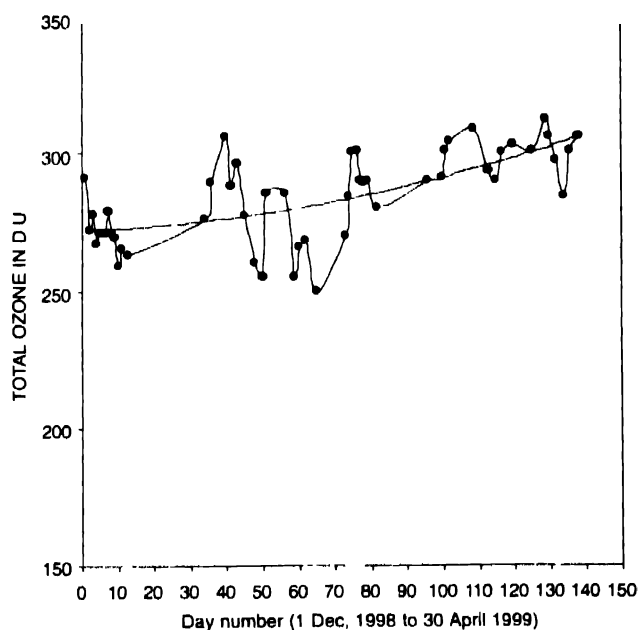


Figure 4. Day-to-day variation for total ozone in the year 1999.

3.1 Monthly mean total ozone:

The monthly mean values of total ozone are calculated and are presented in the Table 1. The variation of monthly mean value

of the total ozone is shown in the Figure 5. This graph leads to the following conclusions.

Table 1. The monthly mean total ozone in DU

Sr No	Year	Dec	Jan	Feb	March	April	Average of five months in the year
1	1996	-	259	267	285	285	274
2	1997	267	258	259	305	276	273
3	1998	255	259	277	292	--	270
4	1999	271	277	283	297	301	285

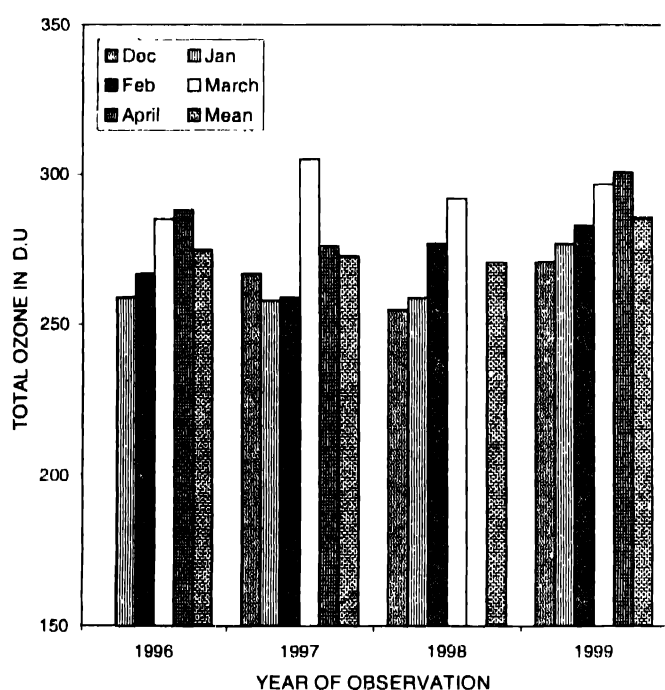


Figure 5. The monthly mean total ozone during the years from 1996-1999

- (i) The monthly mean value of total ozone increases from December to April for years 1996, 1998 and 1999. However for the year 1997, the trend is slightly different and total ozone has large value in the month of December.

This observed trend is similar to that observed for Indian Ozone Mapping Stations at Pune, Kodaikanal and Delhi [23-28].

- (ii) For the year 1997, slightly higher values are noted for total ozone in the month of March.
- (iii) The variation observed in the average of total ozone for five months in a year, has not shown any significant increase or decrease in the total ozone over the place Devgad ($16^{\circ}24'N$, $73^{\circ}26'E$), during the years 1996 to 1999.

3.2 Comparison between results of portable visible spectrometer with the Dobson spectrophotometer:

The total ozone obtained from the Dobson spectrophotometer is measured at Indian Meteorological Department (IMD) Pune, a nearby total ozone measuring station. The solar spectral intensities were measured at Indian institute of Tropical Meteorology Pune with our portable visible spectrometer. Intensities were measured in the two months, May and December of the year 1998, when ozone shows the maximum and minimum values in its annual variation respectively.

During the month of May 1998, the observations of solar spectral intensities were carried out for seven days. Observations were carried out during the morning as well as evening hours. The total ozone densities are calculated for morning as well as evening times and mean total ozone density is taken as the total ozone for that day. During the month of December 1998, the observations were carried out for twelve days and these observations were carried out during morning hours only. From these observations, total ozone densities were computed. The observations were taken only on the clear sky days. Measurements in the month of May, show that portable visible spectrometer has resulted in giving an average 12 percent higher values than that of Dobson spectrophotometer and measurements in the month December 1998 show nearly 10 percent higher values than that measured with Dobson spectrophotometer. From these observations we conclude that the total ozone obtained with the portable visible spectrometer is higher by an amount of 10 to 12 percent than that measured with the Dobson spectrophotometer. This difference is attributed to weak-structured absorption of NO_2 in the spectral range used in the present work and small variation in the absorption cross sections with respect to temperature.

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