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EFFECTS OF THE SOLAR ECLIPSE OF 15 JANUARY 2010 ON DIRECT SOLAR IRRADIANCES, SURFACE OZONE, NO_X, TOTAL OZONE COLUMN AND WATER VAPOUR OBSERVED AT THIRUVANATHAPURAM, INDIA

1. A solar eclipse is not an event which occurs frequently on Earth, where observations can be taken easily. Hence, the effect of this phenomenon on various atmospheric parameters is still uncertain. The solar eclipse of 15, January 2010 visible at one of sites Thiruvanathapuram (8.55º N, 76.77º E) in India provided a unique opportunity to study the observed effects on direct solar irradiance at different wavelengths, surface ozone, NO_x, total ozone column and water vapour. The spectral behaviour of solar radiation reaching the earth's surface during the course of solar eclipse can be studied either with ground based measurements or with the use of radiative transfer model calculations to measure or simulate radiation quantities. Measurements of radiative quantities (Sharp *et al*., 1971; Beletsky *et al*., 1998) and model calculations (Köpke *et al*., 2001) have been performed during various eclipse events.

There are only a few studies (Fernandez *et al*., 1993; Mikhalev *et al*., 1999) that present changes in the solar UV irradiance at Earth's surface during solar eclipse and even few measurements exist of solar limb darkening observations of the extraterrestrial spectrum at UV wavelengths like, *e.g*., (Emde and Mayer, 2007).

However, studies on the solar eclipse induced effects on surface ozone and its precursors are limited particularly over the tropics. A decrease of 18-21% in surface ozone was observed at Ahmedabad during the maximum phase of the solar eclipse of 24 Oct 1995 (Naja and Lal, 1997) and that of 10 to 12 ppb at Robertsgunj (24º42' N, 83º

04' E), compared to its concentration of control days (Dani and Devara, 2002). Recently, Girach *et al.* (2012) showed decrease of surface ozone by 12 and 13 ppb (35% and 52%) over two nearby tropical location, with time lag 40 min and 25 min from the maximum phase of annular solar eclipse, respectively. But at different parts of globe, studies concerning with the eclipse effects on surface ozone were reported by several researchers (Fabian *et al*., 2001; Zanis *et al*., 2007; Zerefos *et al*., 2001; Tzanis *et al*., 2008; David and Nair, 2011). The changes in solar radiation during the solar eclipse may affect the tropospheric or surface ozone and NO_2 in several ways. The surface ozone may be directly affected by the photolysis rate constants changes and indirectly by NO_x and HO_x budget modifications. As a result, the NO destroys ozone forming NO_2 through photolysis. The fast response in tropospheric ozone concentration to the solar eclipse may be clearly identified in polluted sites (Tzanis *et al*., 2008). It is well known that surface ozone forms in the presence of sunlight by chemical reaction between Volatile Organic Compounds (VOCs) and nitrogen oxides both of which are emitted by human activities such as fossil fuel burning as well as by natural sources.

Several earlier studies have examined possible effects of a solar eclipse on the total ozone column (Bojkov, 1968; Khrigian and Kuznezov, 1965; Osherovich *et al*., 1974; Mims and Mims, 1993; Chakrabarty *et al*., 1997; Zerefos *et al*., 2001; Kazadzis *et al*., 2007). (Bojkov, 1968) reported results from Dobson Spectrophotometer observations performed in Sofia, Bulgaria during the solar eclipse of May 1966 and concluded that an increase of 14 Dobson units (DU) was observed at the maximum phase of the eclipse. In that paper a review of total ozone measurements during solar eclipse was presented, and it was emphasized that similar results were also reported in other studies based on Dobson ozone observations (Stranz, 1961). Other studies, however, in which different instruments were used for determination of total ozone have shown different results as to the sign and the magnitude of total ozone changes during a solar eclipse (Khrigian and Kuznezov, 1965). More recently, Kazadzis *et al*., 2007 reported that total ozone measurements performed with a Microtops Sunphotometer during the solar eclipse of 29 March 2006 over Kastelorizo, Greece, showed 30-40 DU lower on the day of eclipse than the day before. During the course of the eclipse, gradual decrease in total ozone followed by a symmetric increase after totality. Chakrabarty *et al*., 1997 reported that total ozone measurements performed with a Dobson spectrometer during the solar eclipse of 24 October, 1997 over Ahmedabad, India, showed sharp fall in the ozone 10 minutes before the maximum obscuration of the sun, followed by a sharp rise 10 minutes after. (Mims and Mims, 1993) showed observations using a portable filter radiometer during the solar eclipse of 11 July, 1991. They reported the occurrence of two ozone minima as well as two maxima on either side of totality. It should be noted that the majority of these studies note that conventional photochemical and dynamical processes could not explain the observed fluctuations.

Measurements of water vapour during solar eclipse have been discussed in various studies (Chimonas, 1973; Kunhikrishnan and Murthy, 1982; Reddy, 1982; Venkatachari *et al*., 1982; Niranjan and Ramesh Babu, 1993; Jain *et al*., 1997; Bose *et al*., 1997). On the basis of measurements of water vapour, they have explained possible reasons of generation of gravity waves during eclipse events. In this paper, we investigate the effects of solar eclipse of 15 January 2010 on direct solar irradiances at different wavelengths, surface ozone, total ozone column, secondary data of NO_x and water vapour at Thiruvanathapuram, a costal city of India.

2. Direct solar irradiance, total ozone column and water vapour were measured at National Institute of Interdisciplinary Science and Technology (NIIST), Thiruvanathapuram (8.55º N, 76.77º E; 3 m m.s.l.). It is capital city of Kerala along the west cost of India. During the period (December to March), the prevailing atmospheric circulation in the lower troposphere is primarily from the inland continental region directed towards the ocean, constituting a continental airmass type. This flow is generally dry because there winds arrive from the dry continental interiors. The minimum temperatures are, in general ranges from 18 to 22 ºC. The relative humidity (RH) generally remains between 40% and 60% signifying the prevalence of a dry environment despite of costal proximity and winds are generally weak $\leq$ 6 ms^{-1}) northerly (Sharma *et al*., 2010) signifying an airmass directed from the interior continental India, which is drier (Moorthy *et al*., 2007). The sky is mostly clear and cloud free.

2.1. Measurements of direct solar irradiance at different wavelengths, total ozone column and water vapour were performed during the solar eclipse of January 2010 by using two different Microtops II – Sun photometers. For total ozone column measurements, a hand held microprocessor–based ozone monitor sun photometer at wavelengths 300, 305, 312, 940 and 1020 nm and for direct irradiance measurements, Microtops II – sun photometer at wavelengths 380, 500, 870 and 936 nm were used. The Microtops II – a five channel hand-held microprocessor-based ozone monitor sun photometer has been operating at National Physical Laboratory, New Delhi and various other sites of India during campaigning and permanent basis at Indian Antarctic station MAITRI for about two decades. The details about the instrument can be found from manual published by Solar Light Company, Inc., 1996, USA. Several studies have been made with the data obtained by this instrument, recently being (Arya *et al*., 2011). The calibration of these instruments requires two sets of calibration constants; the factory calibration (FC) and user calibration (UC). The EC are programmed into the instrument during a calibration process and cannot be modified by the user. The UC are initially set to equal FC but can be individually modified from the instrument's keypad should the user re-calibrate the instrument by his own. The restore calibrations function copies FC into UC restoring the initial configuration of the instrument. Latitude, longitude, date and time are varied according to location. Calibration constants for measurements of irradiance, total ozone column and water vapour are varied based on wavelength values.

Calibration of these instruments is checked on yearly basis. The standard Dobson Spectrophotometer is located at the India Meteorological Department, New Delhi. Data comparison of our instrument with this standard Dobson Spectrophotometer is made once in every 1 or 2 years under identical sky conditions. Calibration factors were also checked before and after the eclipse event and great precautions have also been taken in sun targeting the Microtops throughout the experiment.

The Microtops-II is a five channel hand-held microprocessor-based sun photometer. The instrument is equipped with five optical collimators having a full field view of 2.5°. All the channels are integrated with a narrow-band interface filter and a photodiode appropriate for the particular wavelength range. Each channel looks directly at the solar disc at once when the image of the sun is centered at the cross hairs of the sun target. When the radiation falls onto the photodiodes through collimators, it gives an electrical current proportional to radiant power, which is then amplified and converted into digital form in a high resolution A/D converter. Signals are processed in a series of 20 conversions per second. Of the five channels at 300, 305, 312, 940 and 1020 nm, the first three filter channels were used to derive atmospheric total ozone column and the other two for water vapour (Arya and Jain 1997; Jain, 2001; Ghude *et al*., 2005; Arya *et al*., 2011).

These instruments measure the signals at different wavelengths in mV, from which absolute irradiance in Wm^{-2} is obtained by multiplying the signal measured in (mV) with the calibration factor measured in $[Wm^{-2} \times (mV)^{-1}]$. The calibration constants for studied irradiances at 380, 500, 870 and 936 nm in this paper, the calibration constants are 1.994×10^{-3}, 2.231×10^{-2}, 1.240×10^{-2} and 5.691×10^{-3} $[Wm^{-2} \times (mV)^{-1}]$ respectively.

Surface ozone measurements were also carried out at Thiruvanathapuram, India using an (T-API) - make Ozone Analyzer (Model 400E) during the solar eclipse day and a day latter. The details of the analyzer are given elsewhere (Jain and Arya, 2001).

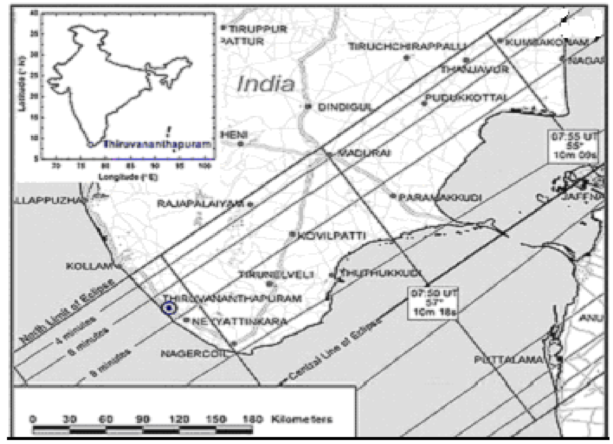


Fig. 1. Path of annular solar eclipse over Thiruvanathapuram on 15 January, 2010

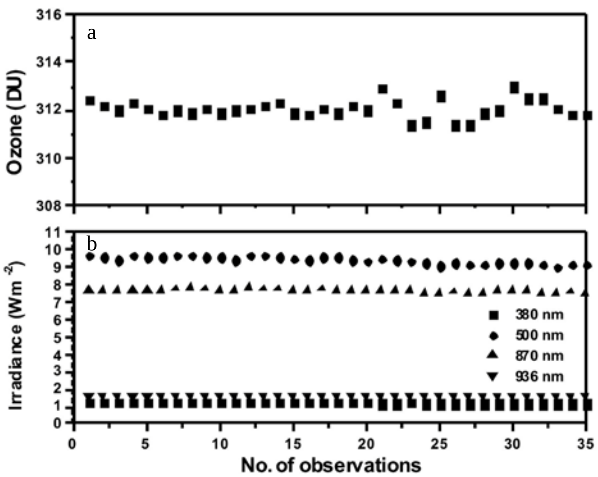
TABLE 1

Data of the eclipse timing at Thiruvanathapuram

Status of eclipse	Time (IST)
Beginning of eclipse	11:15
Maximum solar coverage (92%)	13:20
End of eclipse	15:30

Meteorological parameters, like, temperature, relative humidity, wind speed and solar radiation were recorded by using calibrated portable Weather Logger (M/s. Rain Wise Inc., Bar Harbor, Maine).

3. The direct solar irradiance at different wavelengths, total ozone column and water vapour were measured for the period of 14-16 January, 2010 at Thiruvanathapuram during the solar eclipse campaign. We tried to determine the possible effects of eclipse on direct solar irradiance, total ozone column, surface ozone, NO, NO_2 and water vapour in the present work. At Thiruvanathapuram, the maximum obscuration of the sun was ~92%, which occurred at 1320 hr (IST). It was longest annular solar eclipse of the millennium (Sharma *et al*., 2010). The timing of the different phases of eclipse for the specific location is given in Table 1 and the path of solar eclipse over Thiruvanathapuram is shown in Fig. 1.



Figs. 2(a&b). (a) Rapid measurements of column ozone by using Microtops-II sun photometer (b) Direct solar irradiance at 380, 500, 870 and 936 nm wavelengths using Microtops-II sun photometer

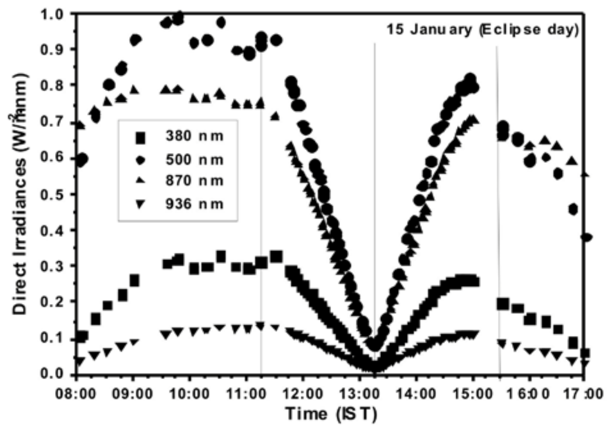


Fig. 3. Direct solar irradiance on the eclipse day at different wavelengths measured with Microtops-II Sun photometer

TABLE 2

Performance of the Microtops-II Sun photometers

Measured parameters	Standard deviation (%)
Irradiance 380 nm	0.03
Irradiance 500 nm	0.20
Irradiance 870 nm	0.08
Irradiance 936 nm	0.02
Ozone	0.37

Microtops-II Sun photometer observations are susceptible to error due to filter degradation and thus require periodic calibration on at least year basis. We have checked the repeatability and precision of the instruments by taking 35 rapid observations at about every 12 s on a day of cloudless-sky condition at noontime. The data given in Fig. 2 gives an idea of the results of these measurements on ozone and on irradiances at 380, 500, 870 and 936 nm wavelengths. The standard deviation for each of these measurements is shown in Table 2. It appears that the repeatability of the data by the instruments is better than 0.2% for direct irradiance and ~ 0.4% for column ozone.

The spectral measurements of direct solar irradiance were performed by Microtops-II Sun photometer. Spectral width for Full Width at Half Maximum (FWHM) of observed wavelength band for all five channels of this instrument are taken as 4, 10, 10, 10, 10 nm. The direct irradiances at 380, 500, 870 and 936 nm during the eclipse are shown in Fig. 3. The black vertical lines represent the start of the eclipse, maximum phase and the end of eclipse. During the maximum phase, decrease in direct solar irradiance was observed at all wavelengths but at 380 nm it showed a stronger decrease compared to other wavelengths. The percentage decrease of direct irradiance at 380, 500, 870 and 936 nm reached 93.94%, 91.30%, 88.73% and 84.61% respectively at the maximum phase of the eclipse. This may be due to sun disc covered by moon on the occasion of the eclipse, resulting decrease in solar irradiance. Except for the decrease in irradiance due to the eclipse, the main change in the irradiance is due to changes in the solar zenith angle.

The observed surface ozone concentration on the eclipse and control days along with solar radiation on eclipse day at the urban site of Thiruvanathapuram are illustrated in (Fig. 4). The effects of solar eclipse on surface ozone were investigated with respect to eclipse maximum and control day of 16 January 2010. During control day, surface ozone concentration started to increase in the morning hours, decreased just before the starting noon hours and then again started to increase which is continued during noon hours, *i.e.*, up to around 1320 hr IST. After attaining its maximum value of ozone, it's started to decrease till the observations of the day. Decrease just before noon hour, *i.e.*, around 1100–1200 hrs IST, may be due to cloudy condition. The daytime higher surface ozone values during normal day are because of photochemical production, which is typical feature of an urban site (Naja and Lal, 1996). On eclipse day, ozone concentration also starts increasing in the morning hours and continued to 1120 hrs IST. It should be noted that decrease in ozone did not start with the first contact at Thiruvanathapuram as it can be seen in (Fig. 4). Ozone continued to increase reaching 52.9 ppb around at 1120 hrs IST and then started decreasing slowly showing a deep minimum. As eclipse progressed, ozone attained

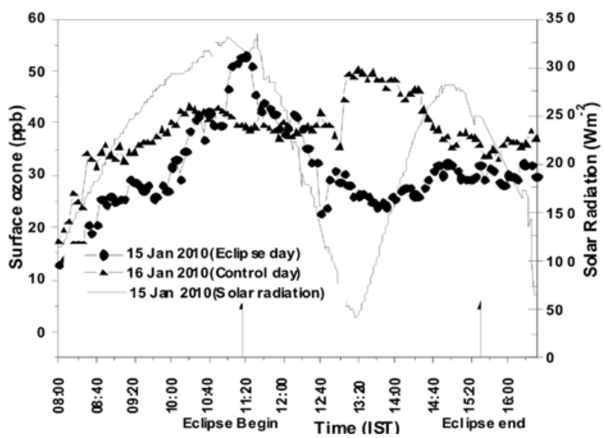


Fig. 4. Surface ozone variation on eclipse and control days along with solar radiation on eclipse day

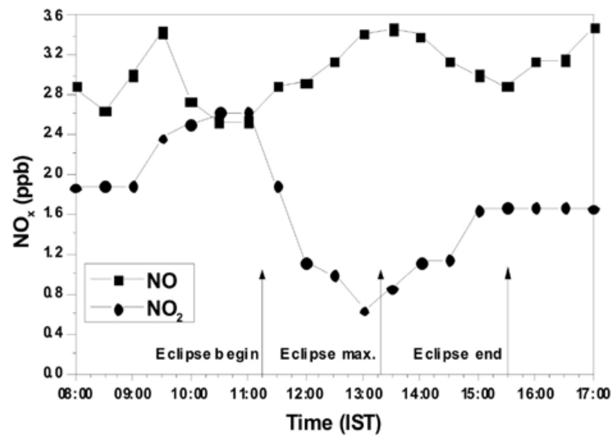


Fig. 5. The partitioning of NO and NO_2 in NO_x on the eclipse day

its minimum value of 24 ppb around 1350 hr IST (after maximum phase of the eclipse) with time lag of ~30 minutes. After that ozone started recovering and reached 32 ppb at 1530 hr IST. A decrease of 54.6% was seen with respect to the eclipse maximum. The time lag attaining dip represents the slow destruction process of ozone. Due to similar reduction in solar radiation, which is shown in (Fig. 4), is capable to reduce more ozone at observational site. At the same site, ozone recorded to decrease by 20.3 ppb (*i.e*., 49.7%) during the maximum phase of solar eclipse (Sharma *et al*., 2010). While, ozone at another site, Kannur (11.9° N, 75.4° E) in the western coastal belt of India, recorded 57.5% decrease during the eclipse (Nishanth *et al*., 2011). A decrease of 18-21% in surface ozone was observed at Ahmedabad during the maximum phase of the solar eclipse of 24 October, 1995 (Naja and Lal, 1997).

Studies conducted at various locations over the globe have shown that solar eclipse causes changes of different magnitudes and temporal scales in ozone. The observed decrease in surface ozone due to solar eclipse of 24 October 1995 was ~10 to 12 ppbv at Robertsgunj (24° 42' N, 83° 04' E). At Ahmedabad (23.05° N, 72.67° E), decrease in ozone concentration observed at maximum phase of the eclipse of 24 October, 1995 was about 185 to 21% (Naja and Lal, 1997). Ozone decrease of ~8 ppb was observed over Silwood Park, Ascot (51°25' N, 0°41' W) during the eclipse (Abram *et al*., 2000). Model based study by Fabian *et al*. (2001) showed the reduction in net surface ozone production by 4-5 ppbv. The decrease in surface ozone can be attributed to the sudden reduction of solar radiation that affects photochemical reactions. Fabian *et al*. (2001) has also reported an increase of 10 ppb in the ozone concentration during the totality of the eclipse of 11 August 1999, which could be partly explained by photochemistry, which can account for the 30% increase of the species. While the surface ozone measurements showed a decrease of ~10 to 15 ppbv at the urban site, at rural site it did not show any clear effect of eclipse (Zerefos *et al*., 2001). All these studies indicate the influence of other parameters controlling the eclipse produced changes in ozone in addition to direct photochemistry. The present study indicates that at the costal site Thiruvanathapuram, which is relatively unpolluted.

Time lag attaining minimum concentration of ozone in the present study, the similar time lag is also reported at other sites, which was attributed to reasons like slow destruction process, photochemical relaxation time etc. (Tzanis *et al*., 2008).

Surface ozone at any location is controlled by (*i*) photochemical oxidation of precursor gases and (*ii*) prevailing meteorological conditions and dynamics. Solar radiation contributes to tropospheric ozone through several reactions of varying rate constants and pathways. In presence of NO_2, maximum surface ozone in the boundary layer is formed through photochemical reactions given by the equations as under:

$$NO_2 + h\nu \rightarrow O(^3P) + NO \ (\lambda<424 \text{ nm}) \quad (R1)$$

$$O(^3P) + O_2 + M \rightarrow O3 + M \quad (R2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (R3)$$

Excited O (^{1}D) (Photolysis of ozone at (λ < 320 nm) leads to production of excited state O(^{1}D) collides with

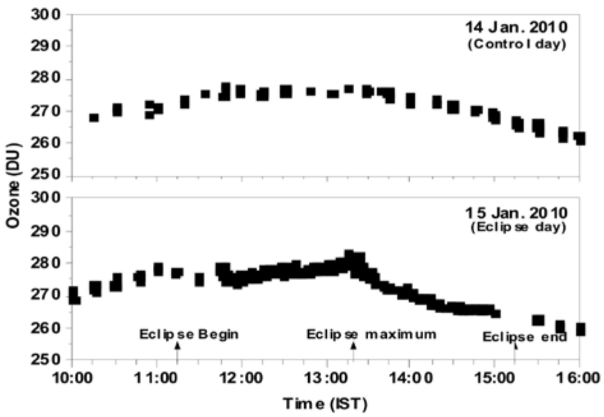


Fig. 6. Total ozone column concentration on eclipse and control days

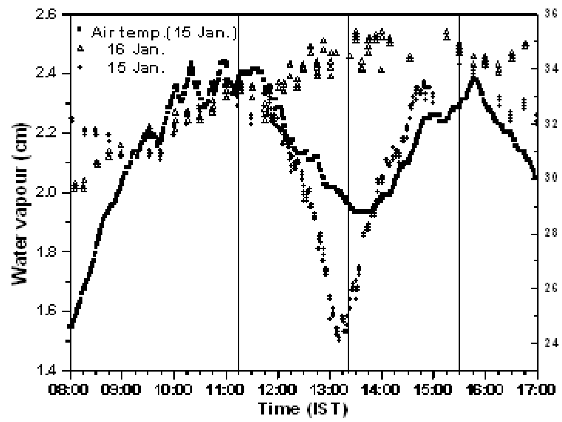


Fig. 7. Total water vapour column variation measured during eclipse and post eclipse days on 15 and 16 January, 2010 respectively along with air temperature on eclipse day at Thiruvanathapuram, India (a) beginning of the solar eclipse (b) solar eclipse maximum, (c) end of the solar eclipse

H_2O producing OH radicals, which converts NO to NO_2 as given by following equations:

$$O(^1D) + H_2O \rightarrow 2OH \quad (R4)$$

$$OH + CO \rightarrow H + CO_2 \quad (R5)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (R6)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (R7)$$

Tropospheric ozone budget is controlled primarily by the $j_{O(1D)}$ and j_{NO2} rate constants and NO_x and HO_2 budgets. The immediate effect of eclipse is the reduction of j_{NO2} which perturbs the steady state condition. The decrease in surface ozone during the eclipse is related to the fall in production rate from the oxidation reactions discussed as above. As maximum obscuration is approached, due to decreasing solar flux, photolysis of NO_2 (reaction R1) stops or weakens and consequently concentration of O_3 will keep on decreasing. In addition, during eclipse period, loss processes including ozone titration by NO_x can also decrease the ozone levels, depending on the availability of NO_x. The time lag between the ozone minimum and the eclipse maximum is partly related to the relaxation time of the photo-stationary state, which is of the order of few minutes (Seinfeld and Pandis, 2006).

To understand the behaviour of (NO_x = NO + NO_2) on eclipse day, data of NO_x were taken from (Sharma *et al.*, 2010) *i.e.*, for same site and plotted (Fig. 5). During the eclipse period, observed NO and NO_2 are clearly indicating that the partitioning of NO and NO_2 in NO_x is well reproduced. However this phenomenon was not discussed in (Sharma *et al.*, 2010). NO_2 started to decrease with progress of the eclipse event and reached minimum during maximum phase shown in Fig. 5.

Measurements of total ozone column were carried out at Thiruvanathapuram using Microtops-II Ozone Monitor-Sun photometer (Solar Light Company, Inc. USA). Microtops-II makes measurement of directly transmitted ground reaching solar UV radiation at 300, 305 and 312 nm and by taking the ratio at two wavelengths for retrieval of columnar ozone. Thus, the measurement of ozone is independent of the absolute amount of radiation.

Eclipse induced changes in total ozone have been reported by several groups using similar and also some time contradictory observations (Bojkov, 1968, in Sofia during eclipse of 1966; Osherovich *et al.*, 1969 and 1974, during the eclipses of 1969 and 1972 respectively; Yadav and Sinha, 1969, in New Delhi during the eclipse of 1966; Beletsky *et al.*, 1998, during eclipse of 1997; Mims and Mims, 1993, during the eclipse of 1991; Chakrabarty *et al.*, 1997, during the eclipse of 1995). It is known that appearance of increased columnar ozone during the eclipse is caused by limb darkening effect of sun. Even applying corrections, many researchers observed eclipse induced changes in columnar ozone and showed that the short-term fluctuations are not an artifact of the instrumental error (Mims and Mims, 1993). Zerefos *et al.*, 2001 suggested that error due to limb darkening effect is less than 1%. Later on, Kzadzis *et al.*, 2007 estimated this correction based on model suggested by Kopke *et al.*, 2001 and found to be much smaller (0.01%) this error. Another possible error in the sun photometric measurements is that caused by diffuse radiation entering the instrument. From the simulations done for this tropical site, the estimated contribution of diffuse radiation for the 2.5° field of view of the instrument is ~2%-3%

(Girach *et al*., 2012). The decrease in total column ozone caused by this diffuse component will not be significant, even though there can be an artifact. However, observed fluctuations can be treated as reliable as reported by (Mims and Mims 1993; Chakrabarty *et al*., 1997). Hence the present measurement using Microtops is used to observe qualitative changes in column ozone associated with the eclipse rather than a quantitative estimate.

Fig. 6 shows total ozone column concentration during the eclipse and control days. Considering upper limits of ozone values at 1147 hrs IST on a day before eclipse, *i.e*., on 14 January, 2010 and at 1314 hrs IST on the day of eclipse, *i.e*., 15 January 2010, total ozone was changed from ~278 to ~260 DU and 283 to ~260 DU respectively. Variation in column ozone was observed increased, before the maximum and decreased after the maximum phase of the eclipse. In the present study, observations cannot be explained by variation in the rates of photochemical and dynamical processes when the sun's disc is slowly covered and uncovered during the eclipse. We suggest the observed variation in ozone during the eclipse is due to some aspect of planetary hydrodynamical theory that bears further investigations.

Fig. 7 shows total water vapour column during eclipse and control days along with air temperature on eclipse day. On control day of the eclipse, *i.e*., 16 January, 2010, concentration of water vapour was observed in the range of 1.35 to 2.54 cm with average value 2.36±0.17 cm. An increased water vapour during morning hours continued to noon hours, *i.e*., up to around 15 00 hrs IST and then it decreased till the observations. On eclipse day, water vapour started to decrease just after beginning the event around (1120 hrs IST) that continued to maximum phase around (1315 hrs IST) and after that it is recovered up to around (1530 hrs IST). It is clear from Fig. 7 that the water vapour concentration decreases as percentage of solar obscuration increases and *vice-versa*. Decrease in water vapour in short period, may be due to some dynamics or conversion of water vapour into liquid water through condensation. This condensation may be due to significant decrease in air temperature during the eclipse (Appu *et al*., 1996). Other possibility is that the spectral variation in solar irradiance might have caused artifacts in column water vapour provided by the sun photometer, which provided the column water vapour content automatically, without considering the eclipse effect.

4. During the annular solar eclipse on 15 January, 2010, the direct solar irradiance at different wavelengths, total ozone column and water vapour were performed at NIIST, Thiruvanathapuram to explore the effect of solar eclipse. Experimental data demonstrated that the solar irradiance, surface ozone, total ozone column, NO_x and water vapour affected by solar eclipse phenomenon. The major results of this study are summarized below.

4.1. The maximum decrease in direct solar irradiance occurred with maximum phase of the eclipse. This may be due to eclipse phenomenon. Except decrease in irradiance due to the eclipse, the main change in the irradiance is due to changes in the solar zenith angle.

4.2. A significant change in surface ozone concentration was seen during the eclipse, the presence of time lag shows the slow process of ozone destruction. The partitioning of NO and NO_2 in NO_x was also observed during the solar eclipse.

4.3. Increased total ozone column was observed, before the maximum and decreased after the maximum phase of the eclipse. This variation is suggested by some aspect of planetary hydrodynamical theory that bears further investigations.

4.4. Water vapour concentration was found to be significantly decreased specifically during the maximum phase of the eclipse.

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