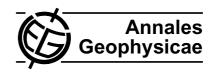
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# Effects of the solar eclipse on 15 January 2010 on the surface O<sub>3</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, CO mixing ratio and the meteorological parameters at Thiruvanathapuram, India

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**Abstract.** In this paper, we present the effect of total solar eclipse on surface O<sub>3</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, CO mixing ratio and the meteorological parameters on 15 January 2010 at Thiruvanathapuram, India. On the day of total solar eclipse (i.e., 15 January 2010), the decrease in mixing ratio of surface O<sub>3</sub> and NO<sub>2</sub> is observed after the beginning of the solar eclipse events (11:15 to 15:30). Decrease in surface O<sub>3</sub> may be due to decreased efficiency of the photochemical ozone formation, whereas, mixing ratio of NO and NH<sub>3</sub> have been changed following the night time chemistry. Surface O<sub>3</sub> reduced to 20.3 ppb after 22 min of full phase of the eclipse. During the solar eclipse period, the ambient temperature and wind speed have decreased, whereas, relative humidity has increased as expected.

**Keywords.** Atmospheric composition and structure (General or miscellaneous)

# 1 Introduction

The solar eclipse is a unique phenomenon gives an opportunity to investigate how the photochemical processes of trace gases in the lower atmosphere react to the comparatively fast solar radiation changes (Tzanis et al., 2008) or when incoming solar radiation is sharply turned off during these events (Amiridis et al., 2007). It gives the opportunity to investigate a great number of parallel phenomenon at different environments (e.g., atmosphere, marine, environment, ecosystems etc.) as well as meteorological variables (Antonia et al., 1979; Zanis et al., 2001; Zerefos et al., 2001; Founda et

al., 2007). The effects of solar eclipse on total O<sub>3</sub> column and stratospheric ozone have been reported by several researchers (Zerefos et al., 2000, and reference therein). Similarly, the studies concerning solar eclipse induced effects on troposphere/surface O<sub>3</sub> and other photo-oxidants i.e., NO<sub>2</sub>, NO etc. are reported by several researchers at different parts of the globe (Srivastava et al., 1982; Abram et al., 2000; Fabian et al., 2001; Zanis et al., 2001, 2007; Zerefos et al., 2001; Tzanis, 2005, 2008). During a solar eclipse event, the variations in total O<sub>3</sub> content has been attributed to the cooling of the atmosphere and therefore, the generation of internal gravity waves (Reid et al., 1994; Zerefos et al., 2007) as well as the alteration of the photochemical balance. The changes in solar radiation during the solar eclipse may affect the tropospheric O<sub>3</sub> and NO<sub>2</sub> in several ways. The mixing ratio of O<sub>3</sub> may be directly affected by the photolysis rate constants changes and indirectly by the NO<sub>x</sub> and HO<sub>x</sub> budget modifications. As a consequence, the NO destroys O<sub>3</sub> forming NO<sub>2</sub> through photolysis. The fast response in O<sub>3</sub> concentration to solar eclipse may be clearly identified in polluted sites (Tzanis et al., 2008). O<sub>3</sub> forms in the presence of sunlight from chemical reaction between hydrocarbon (VOCs) and nitrogen oxides, both of which are emitted by human activities such as fossil fuel burning as well as by natural sources. After sunset, nitrogen oxide compounds undergo reactions that make two new nitrogen containing gases that emit mainly at night. These noctumal nitrogen oxides have the potential either to remove nitrogen from the atmosphere or to store it and re-release it when daytime returns – two possibilities that have vastly different consequences for subsequently ozone formation.



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One of the major problems originated by the air pollution in urban areas is the pollution caused by photochemical oxidants. Among these, O<sub>3</sub> and NO<sub>2</sub> are capable of causing adverse impacts on human health and environment (Lee et al., 1996; WHO, 2000). The oxides of nitrogen (NO<sub>x</sub>) are emitted from several sources viz. thermal power plants, transport, biomass burning and industries, to the atmosphere as NO, which is simultaneously converted into NO<sub>2</sub> and other nitrogenous species leading to formation of several photo oxidants (viz. O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, PAN) and OH<sup>+</sup> (Gupta et al., 2003). Just after sunrise, peroxyacetyl nitrate (PAN) breaks into NO. Because of short lifetime, NO rapidly converts to NO<sub>2</sub> in interaction with O<sub>3</sub> or O<sub>2</sub>. However, due to photochemical reaction, NO<sub>2</sub> breaks into NO and O<sup>1</sup>D, which produces O<sub>3</sub> in the presence of sunlight. After sunset, conversion of NO to NO<sub>2</sub> may be due to chemical interaction with O<sub>3</sub> and dominates when photochemical conversion of NO<sub>2</sub> to NO stops.

Ammonia (NH<sub>3</sub>) is the dominant base in the troposphere that arises from both natural and anthropogenic sources. It is the primary neutralizing agent for atmospheric acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl) and forms inorganic aerosols like (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl which, affects global radiative forcing (Walker et al., 2004). Anthropogenic sources of atmospheric NH<sub>3</sub> are agricultural practices, livestock establishment, roadside vehicles and industrial activities along with natural sources like forest fire and losses from soil under native vegetation. According to photochemical reaction, CO reacts with water vapor producing OH radical and O<sup>1</sup>D in the presence of UV radiation and leads to formation of O<sub>3</sub> in the presence of sufficient NO<sub>x</sub>. Mixing ratio of CO significantly correlated with temperature and humidity (Sharma et al., 2010).

On view of chemical reaction, out of several parameters including surface O<sub>3</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, CO and meteorological parameters such as temperature, relative humidity (RH), wind speed and solar radiation, the mixing ratios of O<sub>3</sub>, NO<sub>2</sub> is expected to decrease and the mixing ratios of NO, NH<sub>3</sub>, CO is expected to increase during the solar eclipse event. Similarly, meteorological parameters i.e., temperature, solar radiation, wind speed is expected to decrease and RH to increase during the solar eclipse event.

In the present work, we examine the behavior of surface ozone, oxides of nitrogen, ammonia, carbon monoxide as well as the variations in meteorological parameters (temperature, relative humidity, wind speed and solar radiation) during the total solar eclipse on 15 January 2010 at Thiruvanathapuram, a coastal city of India. The variations of these trace gases and meteorological parameters during total solar eclipse (TSE) on 15 January 2010 are compared with the characteristics of the same on 14 January 2010 (a day before total solar eclipse) and 16 January 2010 (a day after total solar eclipse).

# 2 Methodology

# 2.1 Description of study site

The mixing ratio of surface ozone (O<sub>3</sub>), oxides of nitrogen (NO<sub>x</sub>=NO+NO<sub>2</sub>), ammonia (NH<sub>3</sub>), carbon monoxide (CO) and meteorological parameters (temperature, RH, wind speed and solar radiation) were measured at National Institute of Interdisciplinary Science and Technology (NIIST), Thiruvanathapuram (8.55° N; 76.77° E; 3 m m.s.l.). It is a capital city of Kerala along the west coast of India. Being a tropical, coastal location, it is situated close to the geographical equator and seasonal changes are not as perceptible at Thiruvanathapuram as at the temperate latitude. During 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 these winds arrive from the dry continental interiors and will be richer in continental pollutants and originated from significantly anthropogenic. The minimum temperature are, in general, ranges from 18 to 22 °C and the diurnal variation (difference between maximum and minimum temperature) in temperature exceeds 15 °C on an average, and go as high as 17 °C at time. The RH generally remains between 40% and 60% signifying the prevalence of a dry environment despite of coastal proximity. The prevailing winds are generally weak ( $<\sim 6\,\mathrm{m\,s^{-1}}$ ) northerly signifying an airmass directed from the interior continental India, which is drier (Moorthy et al., 2007). The sky is mostly clear and cloud free and rainfall is scantly.

# 2.2 Experimental set up

Surface O<sub>3</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub> and CO mixing ratios were measured during total solar eclipse (14 to 17 January 2010) at NIIST, Thiruvanathapuram, India.

An UV-based Ozone analyzer (Model: TECO-49C; M/s Thermo Environmental Instrument Inc. Massachusetts, USA) was used for measuring the surface O<sub>3</sub>. Precision of this analyser is 1 ppb and it was calibrated before and after the solar eclipse events using zero air generator (Model: PAC-003, M/s. Eco Physics AG, Switzerland) and mass flow calibrator (Model: API 700; Teledyne, California). Mixing ratio of NO and NO<sub>2</sub> were measured using NO<sub>x</sub>-Analyzer (Model: CLD88p, M/s. ECO Physics AG. Switzerland) with Photo-catalytic Converter (Model: PLC860 M/s. ECO Physics AG. Switzerland) operating based on chemiluminescence method with an accuracy of ±50 ppt. It was calibrated before and after solar eclipse events using zero air generator and NIST certified NO span gas (500 ppb±5%)

NH<sub>3</sub> mixing ratio was measured using NH<sub>3</sub>-Analyzer (Model: CLD88CYp, M/s. ECO Physics AG, Switzerland) operating based on chemiluminescence method. In this analyzer two catalytic converters of different characteristics

50

40

20

10

0

NO,

(c)

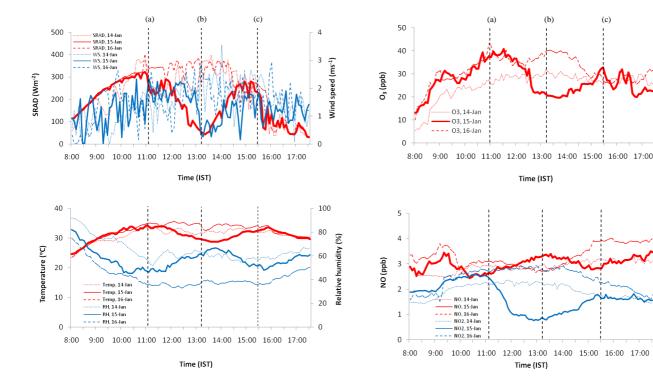


Fig. 1. Solar radiation, wind speed, ambient temperature and relative humidity measured before, during and after the total solar eclipse occurred on 15 January 2010 at Thiruvananthapuram, India, (a) beginning of the solar eclipse, (b) solar eclipse maximum, (c) end of the solar eclipse along with a day before and a day after of the solar eclipse.

Fig. 2. Surface O<sub>3</sub>, NO and NO<sub>2</sub>, measured before, during and after the total solar eclipse occurred on 15 January 2010 at Thiruvananthapuram, India, (a) beginning of the solar eclipse, (b) solar eclipse maximum, (c) end of the solar eclipse along with a day before and a day after of the solar eclipse.

allow sequential detection of NO<sub>x</sub> and NO<sub>x</sub>-amines by converting them into NO. NH3 mixing ratio was calculated from the difference between NO<sub>x</sub> and NO<sub>x-amine</sub>  $(NH_3=NO_{x-amine}-NO_x)$  with an accuracy of  $\pm 50$  ppt.

CO was measured using non-dispersive infrared (NDIR) gas filter correlation analyzer (Model: 48CTL; M/s Thermo Environmental Instrument Inc. Massachusetts, USA). The lowest detection limit of this analyzer is 20 ppb.

In addition, the meteorological parameters such as temperature, relative humidity (RH), wind speed, wind direction and solar radiation were recorded using calibrated Portable Weather Logger (M/s. RainWise Inc., Bar Harbor, Maine).

The total solar eclipse on 15 January 2010 started at 11:15 (Indian Standard Time, IST) and reached the maximum solar coverage (92%) at 13:20 (IST) and ended at 15:30 (IST) at Thiruvanathapuram. It was the longest annular solar eclipse of the millennium with a maximum length of 10 min 4 s.

Sampling inlets of all analyzers and the portable weather logger were stationed at 6 m height (above the ground) and same location. These analyzers were operated continuously for the period of 14-17 January 2010. We have collected the mixing ratio of O<sub>3</sub>, NO, NO<sub>2</sub> NH<sub>3</sub> and CO at 1 mintime resolution during the study period. Statistical analysis of all the data sets was done using standard recommended methods.

# 3 Results and discussion

The mixing ratio of surface O<sub>3</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, CO and meteorological parameters were measured for the period of 14–17 January 2010 at Thiruvanathapuram. It is to be noted that total solar eclipse event was on 15 January 2010.

Figures 1–3 represent the variation of surface ozone, NO, NO<sub>2</sub> NH<sub>3</sub>, CO and meteorological parameters on 14-16 January 2010. On pre-eclipse day (14 January 2010) the average mixing ratio of surface  $O_3$  is recorded as  $22.13\pm6.31$  ppb with a range between 3.5 and 33.7 ppb during day time period (Fig. 2). The variation of surface ozone at Thiruvanathapuram as reported by Nair et al. (2002) earlier is characterized by high  $O_3$  level ( $\sim$ 27 ppb) during daytime and low (about  $\sim$ 7 ppb) during late night and early morning hours. The daytime increase in O<sub>3</sub> mixing ratio is basically due to photoxidation of precursor gases, like CO, CH<sub>4</sub>, and other hydrocarbons in the presence of sufficient amount of NO/NO<sub>x</sub>. Boundary layer processes also play important role in determining the O<sub>3</sub> level by convective mixing of the O<sub>3</sub> poor air of the surface layer and the O<sub>3</sub> rich air at the higher heights.

On pre-eclipse day, the mixing ratio of NO and NO2 ranges from 1.95 to 3.87 ppb and 0.42 to 2.39 ppb with an average value of 2.92 and 1.91 ppb, respectively. The average mixing ratio of ambient NH3 is recorded as

Table 1. Average concentration of surface  $O_3$ , NO,  $NO_2$ ,  $NH_3$ , CO, solar radiation, ambient temperature and relative humidity (RH) before, during and after the solar eclipse event with time lag from mid eclipse at Thiruvanthapuram, India.

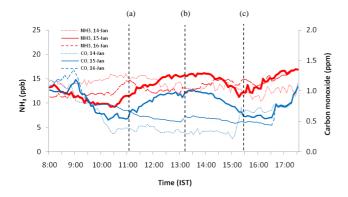
Solar eclipse	O <sub>3</sub> (ppb)	NO (ppb)	NO <sub>2</sub> (ppb)	NH <sub>3</sub> (ppb)	CO (ppm)	Solar radiation (W m <sup>-2</sup> )	Temp (°C)	RH (%)
11:10 11:15–15:30 15:35 Maximum	40.81 25.86 29.72 -20.5	2.59 3.09 2.84 0.97	2.52 1.19 1.64 -1.57	11.49 14.79 12.13 4.05	0.70 0.87 0.59 0.42	309.01 175.02 224.71 -258.2	33.30 31.12 32.31 -3.8	48.71 57.45 52.10 16.2
effect/changes	$(22)^{a}$	(11)	(6)	(12)	(21)	(9)	(20)	(35)

<sup>&</sup>lt;sup>a</sup> Value in parentheses are time lag from mid eclipse (in minutes)

Table 2. Percentage changes in surface  $O_3$ , NO,  $NO_2$ ,  $NH_3$ , CO, solar radiation, ambient temperature and RH in compared with the mixing ratios just before the solar eclipse event at Thiruvanthapuram, India.

Time	O <sub>3</sub>	NO	$NO_2$	NH <sub>3</sub>	CO	Solar radiation	Temp	RH	
12:00	-1.8	12.7	-59.0	20.1	28.0	-29.9	-0.5	1.3	
13:00	-40.8	26.9	-69.0	33.8	36.6	-64.7	-8.6	20.5	
14:00	-45.5	26.2	-56.3	39.2	38.9	-62.5	-13.3	34.9	
15:00	-31.7	13.9	-38.1	16.4	0.1	-15.0	-5.1	16.0	
Mixing ratio (ppb)									
11:10	40.81	2.59	2.52	11.49	$0.70^{a}$	309.1	33.3	48.7	

a value in ppm



**Fig. 3.** Ambient NH<sub>3</sub> and CO measured before, during and after the total solar eclipse occurred on 15 January, 2010 at Thiruvananthapuram, India, (a) beginning of the solar eclipse, (b) solar eclipse maximum, (c) end of the solar eclipse along with a day before and a day after of the solar eclipse.

14.39±1.47 ppb with maxima of 21.96 ppb and minima of 1.06 ppb. The median value of NH<sub>3</sub> at Cochin (9.58° N, 76.73° E, m.s.l.~01 meter), which is closest point to Thiruvanathapuram (Carmichael et al., (2003) is of the order of 19 ppb matches with present reported value. Over Arabian Sea, the NH<sub>3</sub> mixing ratio is of the order of 0.4–0.6 nmol/mol as reported by Gibbs et al. (1999) but it is very low as compare to the present value at Thiruvanathapuram. The mixing ratio of ambient CO recorded as ≤1 ppm on pre-eclipse day.

The variation in mixing ratios of these trace gases depends on the changes in the meteorological condition (Figs. 1–3) and source strength of the locations during the study. The average temperature is recorded as  $30.9\pm2.4\,^{\circ}\mathrm{C}$  with a range of 24.9 to 34.1 °C, whereas, average RH is recorded as  $65.8\pm10.5\%$  with a range of 50.1 to 93.0% during the study. The surface solar radiation ranges from 20.1 to 393.2 W m<sup>-2</sup> with an average value of  $207.3\pm101.2\,\mathrm{W}\,\mathrm{m}^{-2}$ .

The mixing ratios of these trace gases has been varied significantly before, during and after the total solar eclipse period as given in Table 1 as well as time lag of these parameters occurrence with respect to full phase of solar eclipse. Percentage changes in mixing ratios of these trace gases (O<sub>3</sub>, NO, NO<sub>2</sub> NH<sub>3</sub> and CO), meteorological parameters are summarized in Table 2.

On the day of solar eclipse i.e., 15 January 2010 the mixing ratio of  $O_3$  (40.8 ppb) decreases rapidly with the beginning of the solar eclipse period i.e., 11:15 IST and reached at minimum 20.3 ppb (Fig. 2) on 13:37 IST (with time lag 22 min). The mixing ratio of  $O_3$  started to increase again till increasing of solar radiation. Similar trend was observed in the case of solar radiation (Fig. 1). The above behavior of surface  $O_3$  during the solar eclipse may be related to photochemical process due to gradual decrease in the solar radiation affecting the photochemical reactions within the planetary boundary layer (Amiridis et al., 2007). The variations in mixing ratio of  $O_3$  before, during and after the solar eclipse suggest that

the influence of the total solar eclipse was manifested with a certain delay and lasted almost four hours. Increasing trend of ambient CO mixing ratio was observed during the solar eclipses (Fig. 3) might be due to reduction photochemical reaction and low  $O_3$  formation. The changes in mixing ratio of  $O_3$  during eclipse is expected because the mixing ratio of  $O_3$  near the surface is closely linked with the availability of precursor gases and the prevailing meteorological conditions (Nair et al., 2002).

On 15 January 2010, before solar eclipse started, the ambient mixing ratio of NO<sub>2</sub> is recorded as 2.52 ppb on 11:10 IST. NO<sub>2</sub> mixing ratio has started to decrease with advance of the solar eclipse event and reached minimum to 0.78 ppb (Fig. 2) with a time lag of 6 min after the full phase of eclipse. The mixing ratio of NO<sub>2</sub> during total solar eclipse period has decreased by -69.0% as compared to the mixing ratio of  $NO_2$ before the eclipse event started (Table 2). Generally, the mixing ratio of NO2 increases due to balance between photochemical destruction of NO2 and chemical reaction of NO with O3. After sunrise, peroxyacetyl nitrate (PAN) breaks into NO in sunlight. Because of short lifetime, NO rapidly converts to NO<sub>2</sub> in interaction with O<sub>3</sub> or O<sub>2</sub>. In the present case, the mixing ratio of surface ozone decreases due to gradual decrease of solar radiation and may lead to decrease the mixing ratio of NO<sub>2</sub>. On the other hand, the mixing ratio of NO (2.29 ppb) has increased with the decreasing of solar radiation before full phase of eclipse event and decreased with the increase of the solar radiation (Figs. 1–2) after the full phase of eclipse event. The changes might have followed the behavior of the night time chemistry during the eclipse event (Founda et al., 2007; Gerasopoulos et al., 2008).

On the day of eclipse, the maximum ambient mixing ratio of NH<sub>3</sub> is recorded during solar eclipse (11:30 to 15:30 IST) and minimum before and after the solar eclipse (Fig. 3) with a time lag of 12 min after the full phase event. The behavior of the mixing ratio of the ambient NH3 during solar eclipse might have followed the night time chemistry (Sharma et al., 2010). Cadle et al. (1982) and Singh et al. (2001) also reported higher mixing ratio of atmospheric NH3 during the night time over rural area and suburban area respectively. Negative correlation between surface NH<sub>3</sub> mixing ratio and ambient temperature (Sharma et al., 2010) may be attributed to higher NH<sub>3</sub> mixing ratio during night. It is expected that the ambient NH3 has started to increase after the solar eclipse maximum, and it may be attributed to the cooling and stabilizing of the atmospheric boundary layer or night time chemistry (Antonia et al., 1979; Amiridis et al., 2007; Gerasopoulos et al., 2008). However, significant lowering of mixing height during eclipse time may also be attributed to the higher mixing ratio of NH<sub>3</sub>.

Figure 1 shows the temporal variation of the solar radiation, ambient temperature, relative humidity and wind speed on the day of pre-eclipse, day of solar eclipse and the day after the solar eclipse. Ambient temperature close to the surface has decreased from 33.3 °C to 29.5 °C during the total

eclipse event and after the full phase of eclipse, it has began to increase abruptly. The amplitude of temperature dropped by 3.8 °C with a time lag about 20 min after the full phase of eclipse. Similar results were also reported by several researchers (Zerefos et al., 2001; Tzanis, 2005, 2008; Zanis et al., 2007; Founda et al., 2007). Relative humidity has started to increase at 11:15 IST as the decrease in temperature reaching a maximum at the end of the solar eclipse (Fig. 1). The wind speed has also started to decrease after the beginning of eclipse event and reached at minimum during total solar eclipse. It might be due to cooling and stabilization of the atmospheric boundary. Tzanis et al. (2008) has observed the similar changes in above meteorological parameters during the solar eclipse on 29 March 2006 at Athens, Greece. After the end of the solar eclipse period, all the above mentioned parameters exhibited a tendency to re-gain their earlier pattern on the same day and behave in more or less similar fashion on pre-eclipse day and day after the eclipse (Figs. 1–3).

#### 4 Conclusions

During the annular solar eclipse on 15 January 2010, the measurement of surface O<sub>3</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, CO mixing ratio and meteorological parameters (temperature, relative humidity, wind speed and solar radiation) have been performed at NIIST, Thiruvanthapuram to explore the effect of solar eclipse. The experimental data has demonstrated that the solar eclipse phenomenon has affected the mixing ratio of surface ozone, nitric oxide, nitrogen dioxide, ammonia as well as temperature, relative humidity, wind speed and solar radiation near the ground. The decrease in mixing ratio of surface O<sub>3</sub> and NO<sub>2</sub> is observed after the beginning of the solar eclipse events and lasted for four hours, probably due to decreased efficiency of the photochemical ozone formation, whereas, the increase in mixing ratio of NO and NH<sub>3</sub> might have followed the night time chemistry. As expected, the ambient temperature has decreased, relative humidity has increased and the wind speed has decreased. After the end of the solar eclipse period, all the above mentioned parameters exhibited a tendency to re-gain their earlier pattern on the same day.

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