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Surface ozone measurements at urban coastal site Chennai, in India

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Abstract

The present study was carried out to gain knowledge of current surface ozone concentrations and the effects of meteorological parameters in the highly populated urban area of Chennai, in South India. We have reported measurement results of surface ozone (O_3) and meteorological parameters from 17th March to 10th October 2005. A photometric ozone analyzer continuously recorded the ozone concentrations at this site. The present study deals with the statistical characteristics of daily and monthly mean ozone levels under different meteorological conditions. The highest ozone concentrations were recorded in ESE-SE sectors. The monthly mean concentrations were higher in May (23 ± 14 ppb) and lower in April at this site (10 ± 8 ppb). The maximum hourly ozone concentration reached 69 ppb on 21st April.

Keywords: Surface ozone; Meteorological parameters; Coastal site; Wind direction

1. Introduction

Ozone (O_3) is a secondary pollutant formed in the presence of precursor compounds (nitrogen oxides (NO_x) and volatile organic compounds (VOCs)) and sunlight. Its concentration in the atmosphere is influenced by concentrations of the precursor emissions, meteorology, turbulent mixing, atmospheric chemistry and surface dry deposition (the major removal process). The lifetime of ozone can vary from hours to several days and so it can be transported for long distances. Ozone will be formed at any time in daylight if the precursor concentrations are large enough [1]. The formation of O_3 by photolysis of NO_2 can be presented as:

$$NO + O_3 \rightarrow NO_2 + O_2 \text{ (titration)}$$

$$NO_2 + h\nu \rightarrow NO + O \text{ (NO_2 photolysis)}$$

where the oxygen atom (O) rapidly combines with molecular oxygen (O_2) to produce ozone. This reaction is counterbalanced by titration of NO with ozone.

$$O_2 + O + (M) \rightarrow O_3 + (M) \quad (M = \text{intermediary compound})$$

The process of ozone formation from other precursors like VOCs, CO were reported detail by Sillman, 1999 [2]. However, the possible reaction sequences are very complex, due to the involvement of several hundred VOCs, radicals and NO_x [1]. Thus in a VOC and NO_x polluted atmosphere ozone can be produced.

In recent years, a limited number of surveys have been conducted on surface O_3 over urban sites [3–5] and tropical coastal site [6] in India. Ozone levels at a high altitude site Mt. Abu, India, was estimated to be 33.4 ± 13.3 ppb for the period 1993–2000 [7]. Some modeling studies have been conducted by Debaje and Jadhav [8] and Jain and Kundu [9] over the Indian region. But very little information is available on the surface ozone at Coramandal Coasts of the Bay of Bengal, India [10]. Recent trend in ozone distribution in urban areas in Chennai are shown by Pulikesi et al. [11]. To the best of the author's knowledge, no continuous measurements have been carried out over Chennai's metropolitan area on the Coromandal Coast of the Bay of Bengal, India.

Ozone uptake leads to damage in all types of vegetation mainly on phytotoxic (reduces crop yields), and reduces the

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lifespan of materials (like rubber, painting, etc.) [1]. In the case of human health, ozone induces inflammation in the lungs at high concentrations and triggers asthma attacks in sensitive individuals, hence it is believed it only exacerbates existing disease or predisposes a person to develop disease. It has been reported that it can affect a 4% increase in paediatric asthma rate per 20 ppb increase in ambient ozone concentration [12]. Recent literature also shows that the estimated number of ozone related deaths during the period June–August 2000, 2002 and 2003 in Netherlands were 990, 1140 and 1400, respectively [13]. Further, it is a greenhouse gas absorbs the earth's infrared radiation at 9.6 μm, which is responsible for climate change. As per WHO [14] standards, the allowable limit of primary air quality standard for O_3 is 50 ppb.

Hence, it is essential that information on ozone is available in order to protect human beings and plants from such adverse effects. In particular, it would be highly desirable to obtain measurements in Chennai, where the emission per unit area of NO_x, an O_3 precursor, has been the highest in India in 1995 [15]. Due to its high population density and heavy traffic Chennai can be considered to be one of the most interesting area to investigate ozone concentrations. Data on meteorological parameters on a regional scale are needed. It would be interesting to track the wind evolution from coast to the experimental site in the morning of sunny days. Hence, Meteorological data were collected from Indian Meteorological Department (IMD) and Tamilnadu Pollution Control Board (TNPCB), Chennai.

In this paper, we present the hourly measurements of ozone and study the statistical characteristics of surface ozone according to meteorological parameters. We will also compare our data with those obtained from other places in India.

2. Location of site and measurement techniques

2.1. Description of the sampling site

India is a tropical country. The southern part of India is a peninsula surrounded by three major seas. Chennai city is the capital of Tamil Nadu state in south India and is located in the eastern coast. It is the fourth largest city in India has a large population of 7.45 million [16] and covers an area of 1180 km^2. The ozone monitoring station has been installed in the southern part of Chennai at the Alagappa College of Technology, Anna University (latitude 13°04N; longitude 80°23E). It is located 3.5 km away from the Bay of Bengal shore. The sampling site is adjacent to the Cancer Institute, Adyar River and Indian Institute of Technology, Madras, and tourism spots, namely, Children's park and Gandhi Mandapam, which receive a large number of visitors every day. Many heavy industries are located in the N-NE sector about 30 km away from the observation site. The nearest emission sources are heavy traffic in the southern and eastern parts of the observation site. Measurements have been performed on the terrace of the college above a three-floored building from March 17th to October 15th 2005. Fig. 1 shows the location of O_3 and metrological observation sites.

2.2. Measurement techniques

2.2.1. Ozone monitoring

An Environment S.A Module O_3 42 M ozone analyzer was used to measure O_3 concentrations at the site. The principle is based on absorption of UV radiation at 253.7 nm by ozone molecules. A zero and span check was done once a week using the analyzer's built-in ozone generator. The minimum detectable limit of the instrument is about 1 ppb with response time of 50 s. The monitor was kept on the first floor of the building. Air was continuously drawn via Teflon tube (6 m-length and 0.7 dia), by the analyzer's internal pump at a flow rate of 1 l/min. The instrument had an in-line particulate filter to prevent particles from entering the instrument. The analyzer continuously monitors the O_3 concentration and stores 2-min averages in a RAM data logger as well as 15-min averages at the end of this time period. The 15-min average is also displayed on the liquid crystal display (LCD) screen of the analyzer and then noted separately. Each hourly ozone concentration is the average of four 15 min measurements taken during an hour and is reported as the hourly concentration. Hourly ozone concentrations are reported in the nearest ppb.

2.2.2. Meteorological parameters

In combination with the ozone data, monthly mean air temperature, rainfall, wind speed and bright sunshine hours data were collected from the Indian Meteorological Department (IMD), Chennai (Nungambakkam) station (see Fig. 1), which is located 6.5 km away from the monitoring site. Fiber reinforced plastic (FRP) rain guards have been used to measure the rainfall.

The other meteorological data like relative humidity and wind direction were collected from the 'Royapuram meteorological station' (TNPCB) (see Fig. 1), which is located 12.5 km away from the monitoring site. The sensors were fitted at 7 m above ground level. Vane type anemometer was used to measure the wind direction. The minimum significative velocity for Humidity was 1%. According to IMD guidelines, these meteorological data were valid up to 40 km from the monitoring station.

3. Results and discussions

Continuous measurements of O_3 concentration and meteorological variables were carried out from March to October 2005. There were limited number of measurements in the month of May, June and July as the ozone analyzer was used for another field study [11]. The ozone concentrations in Chennai area were statistically analyzed on different time-scales, namely, hourly, daily and monthly mean. We also determined correlation between O_3 concentrations and some relevant meteorological quantities.

3.1. Ozone concentrations

Table 1 shows the maximum, minimum and mean O_3 concentrations from March to October 2005. It indicates that the highest monthly mean O_3 concentration is observed in May (23 ± 13 ppb) than those of the other months. This may be due

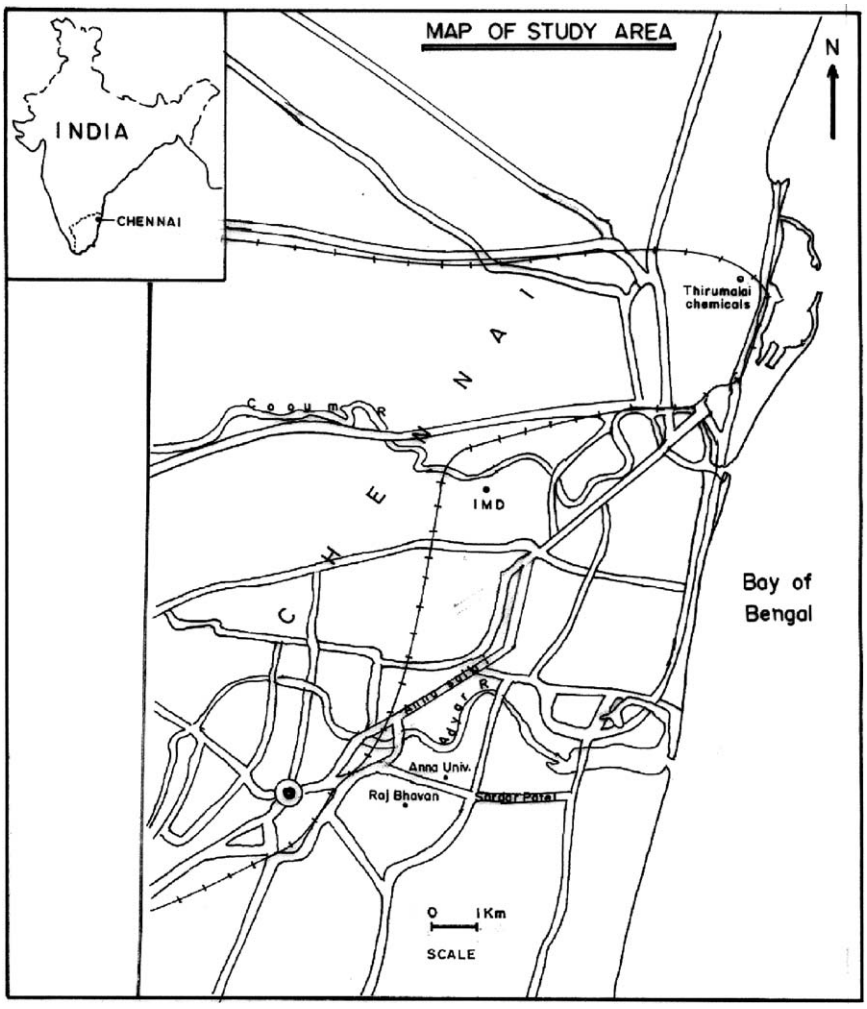

Fig. 1. India with the location of O_3 and metrological observation sites.

to highest maximum temperature of 41.3 °C and lowest monthly total rainfall of 30.9 mm. Earlier studies carried out by Debaje et al. [10] for the period May 1997 to October 2000 also got similar values in the month of May at Tranquebar, a Tropical rural coastal site on the east coast of India. The maximum ozone concentration varies between 30 and 69 ppb, with the lowest in July and the highest in April.

Fig. 2 shows the daily mean and maximum O_3 concentration during March–October 2005. White circle indicates the 24 h mean ozone concentration and the shaded line indicates the daily maximum ozone concentration. The hourly O_3 concentration varied from 1 to 69 ppb. The mean O_3 concentration reaches the highest levels in end of May and first half of June. These concentrations do not exceed the US EPA Standard, i.e. 1 h permissible concentration of 120 ppb. The percentage frequency of the O_3 data exceeded the hourly WHO standard and was 1.12. Similar work reported by Khemani et al. [17] in Pune has indicated a percentage frequency of 3.21. The exceeded values were mostly

Table 1
Monthly details of surface ozone (parts per billion (ppb)) obtained at Chennai from March to October 2005

Months	Mean ± sigma	Maximum	Minimum	Count per hour	Count %
March	12 ± 6	35	1	351	47.5
April	10 ± 8	69	3	736	99.6
May	23 ± 13	66	2	435	58.9
June	20 ± 11	51	4	174	23.5
July	11 ± 6	30	1	187	25.3
August	15 ± 10	60	1	739	100
September	14 ± 10	60	1	699	94.6
October	14 ± 12	50	2	157	24.2

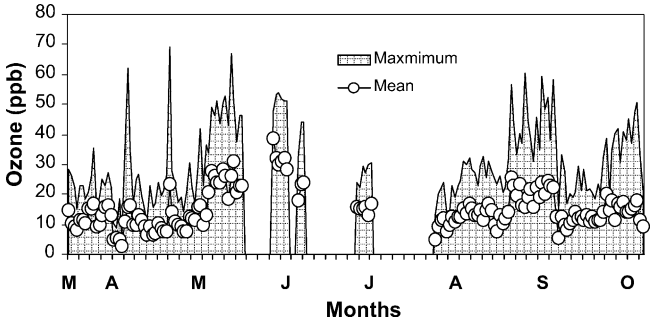

Fig. 2. Record of daily maximum and mean ozone concentration during 17th March–10th October 2005.

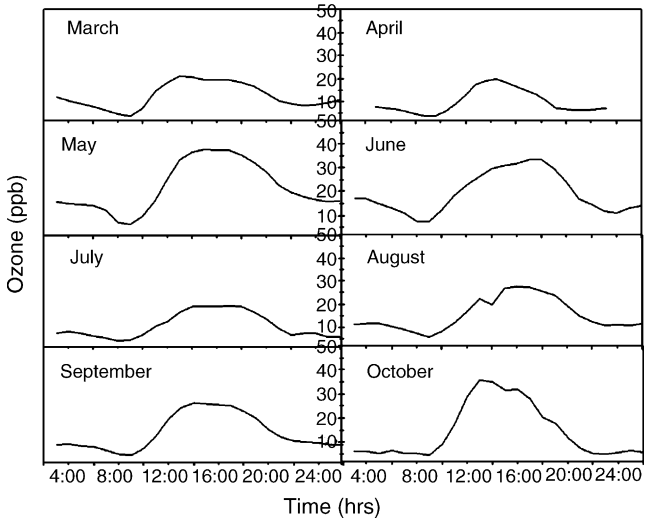

Fig. 3. Diurnal variations of average ozone at Chennai in different months for the period March–October 2005.

observed in the month of May and June. On most of the days, the hourly maximum O_3 concentration was recorded from 11:30 to 15:00 h.

3.2. Diurnal variation

Average diurnal variation of surface ozone in different months for the period May to October 2005 is shown in Fig. 3. Seasonal and diurnal cycle observed in Chennai is typical of most ground surface monitoring sites around the world [2,18,19]. The diurnal cycle is governed by changes in the planetary boundary layer (PBL) and free troposphere, although photochemical production also plays a part. During the daytime, turbulent mixing in the PBL, induced by both wind shear and thermal convection, lead to entrainment of ozone from the free troposphere. In sunny weather the presence of NO_x and VOC emissions may also lead to photochemical production throughout the troposphere and so enhanced ozone concentrations. These processes produce an afternoon peak in ozone concentration when the atmosphere is most turbulent and UV levels are at a maximum (12:00–14:00 h). During the night (20:00–24:00 h) and early morning (5:30–07:00 h) the lower regions of the boundary layer become thermally stratified and stable as the surface cools, greatly reducing entrainment of ozone from the free troposphere. The ozone concentration decreases rapidly as losses to dry deposition are not replenished by mixing from above and photochemical production cannot occur.

3.3. Surface ozone during nighttime and daytime

The data obtained during the period March to October 2005 have been presented in Table 2 indicating the mean O_3 level. The data is relative to the mean O_3 level during nighttime (23:30–02:30 h) and daytime (11:30–14:30 h). The monthly mean O_3 concentration shows a daytime maximum (38 ± 10 ppb) in May and minimum (18 ± 12 ppb) in April, and

Table 2
Mean surface ozone (parts per billion (ppb)) concentrations observed during nighttime and daytime for the period of March–October 2005 at Chennai

Months	Mean O_3 at nighttime (23:30–02:30 h)	Mean O_3 at daytime (11:30–14:30 h)
March	13 ± 4	19 ± 4
April	7 ± 5	18 ± 12
May	16 ± 6	38 ± 10
June	15 ± 3	30 ± 9
July	7 ± 3	20 ± 3
August	11 ± 6	27 ± 9
September	9 ± 4	26 ± 11
October	5 ± 2	32 ± 9

corresponding nighttime maximum (16 ± 6 ppb) in May and minimum (5 ± 3 ppb) in October. The mean O_3 is 26 ppb during daytime and 11 ppb during nighttime. It has been observed that the mean O_3 concentrations during daytime in Chennai are nearly two to three times greater than the mean nighttime O_3 values. This result is comparable with the findings of Debaje et al. [10] who obtained similar data in the coromandal coast of Bay of Bengal (Tranquebar), India. Similarly mean nighttime O_3 concentrations during the present study are high at Chennai as compared to other sites.

3.4. Variation of ozone with meteorological parameters

Fig. 4 shows the monthly mean meteorological parameters, temperature (°C), wind speed (m/s), rainfall (mm) and bright sunshine hours which were collected from surface observatory (IMD) during O_3 monitoring days. Temperature ranging from 22.0 to 41.6 °C, attains a mean value of 38.3 °C in the month of June. Most of the days, relative humidity reaches a maximum of 100% during nocturnal hours when water vapor condenses. The mean wind speed of 9 km/h was recorded in the month of June. It was found to be the maximum compared to the other months. During the bright sunshine hours (8.4 h), maximum ozone level was found to be between 10:00 and 20:00 h in the month of May. A light rain was observed on 3rd–6th April 2005 and 9th September 2005 it was 5.6, 0.4, 30.6, 121.6 and 5.5 mm, respectively. During this 5-day period we recorded low mean ozone concentrations as low as 5 ppb. The low O_3 concentrations are probably due to the reduction in UV radiation resulting in loss of O_3 by titration with local emissions of NO [20].

An influence of wind direction on O_3 concentrations (Fig. 5) was also observed with the highest concentrations recorded for winds blowing from the ESE, SE and SSE sectors correspond to the direction of onshore flow. Ozone concentration has been found to be low above surface of the ocean (open ocean with clean atmosphere) as compared to the land, which may be due to low NO_x concentration [21]. The loss of ozone is about 84% by chemical reactions and remaining 16% is due to dry deposition [22]. However, higher ozone is observed when the wind is from sea. This may be attributed to the chlorine radical (Cl) emitted from salt particle of sea, which oxidizes VOC, almost twice than that of the hydroxyl radical (OH) which promotes the ozone formation at the coastline [23]. Such reactions described may

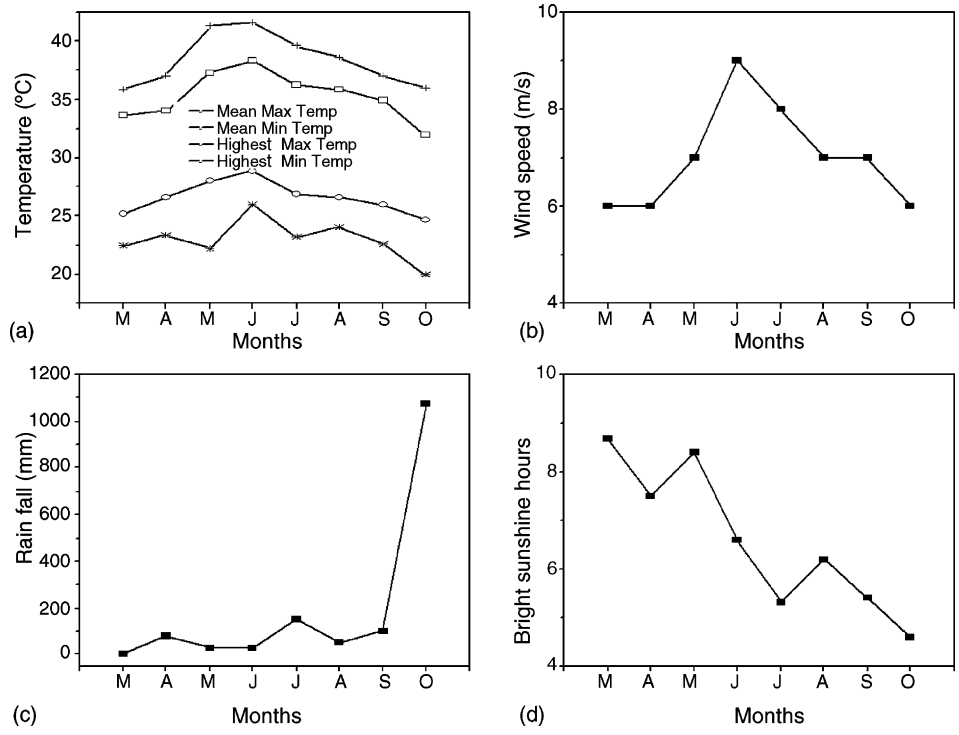

Fig. 4. Average variations of meteorological parameters for the period March–October 2005. (a) Mean surface temperature, (b) mean wind speed, (c) total rainfall and (d) bright sunshine hours.

play a part but VOC concentrations in the air is required to be large enough [1].

Fig. 6 shows the hourly pattern of wind direction with ozone concentration recorded during the period of May 10th–11th. The present study shows the maximum exceedances of hourly O_3 concentration in the above selected days. During this 2-day period, surface winds were very low, indicating the influence of the high-pressure system. In the high-pressure conditions, during the day time ozone production rates by photochemistry probably be enhanced and large amounts of ozone may be entrained from the free troposphere into the boundary layer by convection cells. This is the more likely cause for the largest ozone concentrations being observed on these days [1].

It has been clearly noticed from the Fig. 6 that the high ozone concentrations co-inside with the changes in wind-direction (wd), concentrations where increasing prior to the wd change. The changes in ozone look like typical diurnal cycles driven by boundary layer dynamics, ozone deposition and titration. A southerly to southwesterly wind dominated in the early morning (03.30–06.30), while an easterly to southeasterly wind dominated in the late afternoon (13.00–20.30). We may clearly notice that when wind direction is east southeasterly, O_3 concentrations are systematically at elevated levels. Mean daytime temperatures

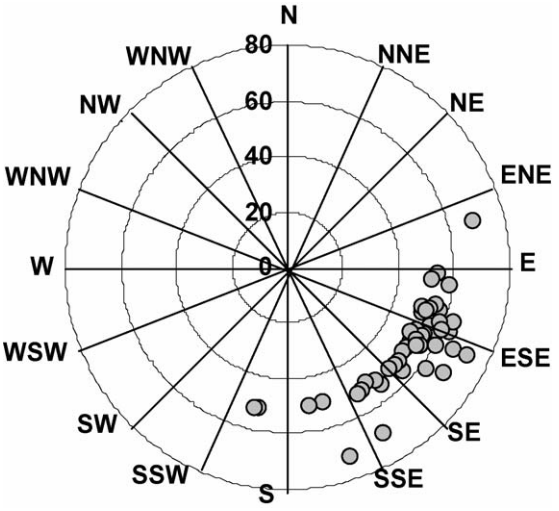

Fig. 5. Ozone concentration scattered polar plot obtained the concentrations are higher than 50 ppb.

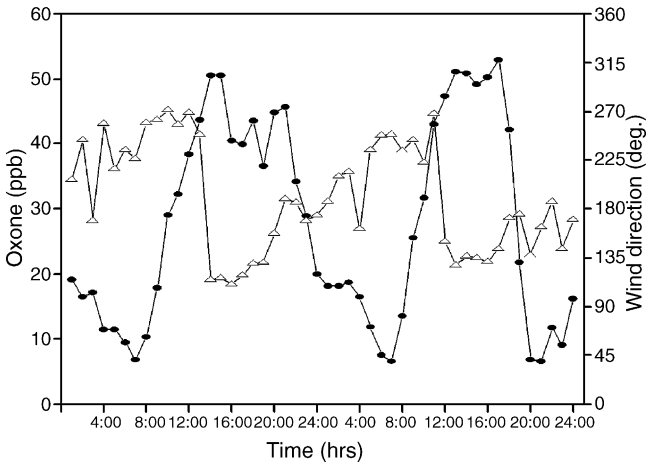

Fig. 6. Ozone concentration (●) vs. wind direction (△) during period May 10–11, 2005.

on that day were found to be approximately 2 °C higher when compared to those on other days of this month.

4. Conclusions

Surface O_3 concentration with meteorological parameters in March–October 2005 has been analyzed. The following conclusion was drawn from the present study. The mean ozone concentrations are higher (23 ± 14 ppb) in May, which may be due to highest maximum temperature of 41.3 °C and lowest monthly total rainfall of 30.9 mm and lower in April (10 ± 8 ppb) month. A strong diurnal variation of surface ozone is observed from a maximum in the afternoon and then minimum in the early morning. Observed concentrations of O_3 during daytime and nighttime were found to be higher when compared to the other sites in India. The measured ozone concentration is affected by the direction of wind. The ozone concentrations higher than 50 ppb were recorded for winds blowing from ESE, SE and SSE sectors. This is probably due to onshore airflow and reduced ozone deposition to the sea surface. The scope of the present study is limited to specific period in a year. However, further extensive study is required on the measurements of O_3 and precursor gases to understand the formation of surface O_3 and to study the seasonal cycles at this site.

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