Occurrence of High Nocturnal Surface Ozone at a Tropical Urban Area

S. Dey, P. Sibanda, S. Gupta, A. Chakraborty

Abstract—The occurrence of high nocturnal surface ozone over a tropical urban area (23° 32′16.99″ N and 87′ 17′ 38.95″ E) is analyzed in this paper. Five incidences of nocturnal ozone maxima are recorded during the observational span of two years (June, 2013 to May, 2015). The maximum and minimum values of the surface ozone during these five occasions are 337.630 μg/m³ and 13.034 μg/m³ respectively. HYSPLIT backward trajectory analyses and wind rose diagrams support the horizontal transport of ozone from distant polluted places. Planetary boundary layer characteristics, concentration of precursor (NO₂) and meteorology are found to play important role in the horizontal and vertical transport of surface ozone during nighttime.

Keywords—Nocturnal ozone, planetary boundary layer horizontal transport, meteorology, urban area.

I. INTRODUCTION

TROPOSPHERIC OZONE (O₃) present in the planetary boundary layer (PBL) is considered as one of the criteria pollutants. It plays a key role in atmospheric chemistry and climate change. Apart from being a greenhouse gas, ozone is a precursor for the highly reactive hydroxyl radical which determines the chemical composition of the troposphere. Ozone variation within the PBL is a complex function of surface emissions and deposition, photochemistry, horizontal transport and interaction with the free atmosphere [1]. The residence time of ozone in the atmosphere is almost 100 days. Ground level ozone is notably exceeding the permissible limit in several regions due to increasing emissions of its precursors from anthropogenic activities.

Ozone shows a prominent diurnal variation with the maximum concentration during the noon and minimum at early morning. But, it is interesting to note that sometimes high level of surface ozone is recorded even after sunset and continues till late night. The presence of high concentration of O₃ during nighttime is termed as nocturnal ozone maximum. Some researchers have focused on the occurrence of nocturnal ozone in different regions of Europe and North America [2]-[4]. The importance of vertical mixing processes for the

vertical dispersion of boundary layer ozone in Maryland, USA was explored [5]. The magnitude, frequency, and time of high nighttime O₃ concentrations were analyzed at Kemaman, Terengganu with respect to the precursors of O₃ such as NO₂, NO, and CO concentration and meteorology [6]. In India, nighttime chemistry of oxides of nitrogen (NOx) and ozone in presence of the NO2–NO3–N2O5 cycle was studied and explained the role of meteorology and transport (both horizontal and vertical) in the nocturnal ozone maxima episodes [7].

The present work focuses on the identification and analysis of nocturnal ozone maxima episodes over a tropical urban area (Durgapur) during the time span of two years (June, 2013 to May, 2015). This study attempts to find the role of PBL phenomena, horizontal transport and meteorology in controlling the nocturnal ozone level near the earth's surface.

II. MATERIALS AND METHOD

The chosen urban area – Durgapur, is situated in the Burdwan district of West Bengal, India. The topography of this area is undulating, with an average elevation of 65 m MSI

The data of concentration of surface ozone at City Center, India (23° 32′16.99″ N and 87′ 17′ 38.95″ E) are collected for the duration of two years (June, 2013 to May, 2015) from the archived data set of WBPCB (Durgapur station) [8]. Fig.1 shows the details of study area.

The data of PBL height, vertical mixing coefficient, and meteorological parameters (temperature, humidity, pressure, wind speed) are collected from the NOAA Air Resources Laboratory (ARL) website [9]. The back trajectory simulation has been done by using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) [10] model and by utilizing the GDAS Meteorological data. The 24-hour back trajectories at three altitude levels (100, 500, and 1500 m AGL) are simulated. Wind rose diagrams are constructed by using software WRPLOT View (Version 7.0.0).

III. RESULT AND DISCUSSION

A. Occurrence of High Nocturnal Ozone

Surface ozone and its precursor (NO₂) show a characteristic diurnal variation [Figs. 2 (a) and (b)]. Ozone concentration starts increasing gradually after sunrise, attains maximum around noontime, and starts decreasing after late afternoon or evening [11], while NO₂ shows the reverse trend. Increase in NO₂ concentration during the morning and evening hours can

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be attributed to combination of anthropogenic emission, boundary layer processes, and local surface wind patterns.

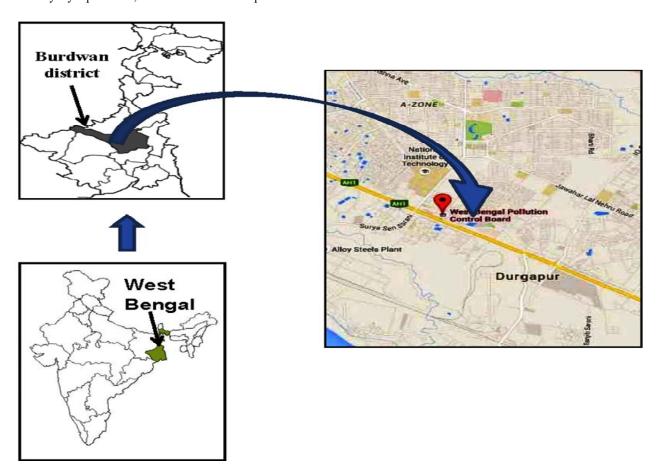
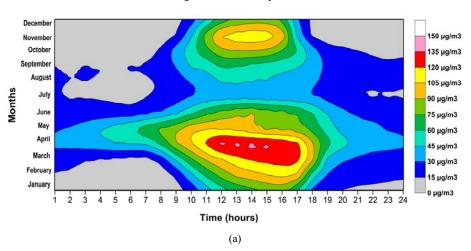


Fig. 1 Details of study area



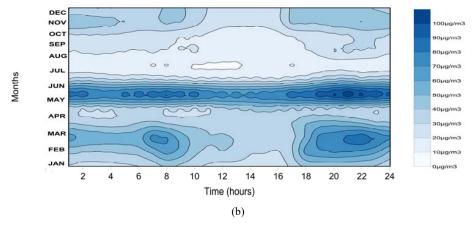


Fig. 2 Diurnal variation of (a) surface ozone and (b) nitrogen dioxide (NO2) during the study period over the chosen urban area

The photoxidation of its precursor gases such as CO, CH₄, NMHCs in the presence of sufficient amount of NO_x increases the daytime ozone concentration and it is a pronounced feature of a polluted urban area [12], [13]. During the noon hours, ozone rich air in the higher heights mixes with the air in the lower height which has low amount of ozone [14]. But, after sunset, the photochemical production of ozone ceases and vertical transport of ozone is inhibited by nocturnal inversion. Loss of ozone by reaction with NO (titration) and dry deposition are othercauses of low ozone concentration during nighttime.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (1)

Apart from NO titration, NO₂ plays a significant role in destruction of nighttime ozone [15].

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
 (2)

$$NO_3 + NO_2 + M \longrightarrow N_2O_5 + M$$
 (3)

The N₂O₅ produced in (3) is found to be thermally unstable which can easily dissociate back into NO₃ and NO₂ radical [7]. Interestingly, substantial amount of ozone is found even after daytime duration. The nocturnal period is found to exist between 19:00 h and 04:00 h (next day) during monsoon and pre monsoon seasons and between 18:00 h and 05:00 h (next day) during the post monsoon and winter seasons. During the

span of two years (June, 2013 to May, 2015), five such incidences were observed on which the average nighttime ozone concentration exceeded the daytime average of ozone before the onset of the nocturnal period. Table I gives the details of average surface ozone concentration during the nocturnal period and during the daytime on the days before and after the nocturnal episode. The maximum and minimum values of the surface ozone during these occasions are 13.034 $\mu g/m^3$ and 337.630 $\mu g/m^3$, respectively. The day with the highest concentration of daytime and nighttime ozone has also been identified (09.12.14). On 09.12.14, the range of ozone concentration during the nocturnal period lies between 169.780 $\mu g/m^3$ to 287.370 $\mu g/m^3$.

B. Role of Boundary Layer Phenomena, Horizontal Transport, Precursor (NO_2) and Meteorology

Occasional high level of nocturnal ozone might be the manifestation of combined effects of boundary layer characteristics, horizontal transport, concentration of one of the precursors (NO₂) and meteorology. Table I portrays the average surface ozone concentration during the nocturnal period and during the daytime on the days before and after the nocturnal episode.

The diurnal variation of PBL height and vertical mixing coefficient on the days with the nocturnal ozone maxima and the following day are given in Tables II and III, respectively.

TABLE I

AVERAGE SURFACE OZONE CONCENTRATION DURING THE NOCTURNAL PERIOD AND DURING THE DAYTIME ON THE DAYS BEFORE AND AFTER THE NOCTURNAL EPISODE

Dates	Average ozone concentration during the daytime before the onset of nocturnal period (µg/m³) [Date]	Average nighttime ozone concentration during the nocturnal periods (µg/m³)[Date of overlapping period]	Average ozone concentration during lapse of nocturnal period (μg/m³)[Date]
19.08.13	28.129 [19.08.13]	31.523 [19.08.13-20.08.13]	35.062 [20.08.13]
21.08.13	27.618 [21.08.13]	31.046 [21.08.13 - 22.08.13]	43.756 [22.08.13]
30.09.13	22.145 [30.09.13]	22.146 [30.09.13 -01.10.13]	22.555 [01.10.13]
17.09.14	63.764 [17.09.14]	88.741 [17.09.14 - 18.09.14]	106.235 [18.09.14]
02.01.15	35.447 [02.01.15]	36.748 [02.01.15 - 03.01.15]	48.470 [03.01.15]
*09.12.14	232.267 [09.12.14]	228.210 [09.12.14 -10.12.14]	78.882 [10.12.14]

^{*} Day with the highest daytime and nighttime ozone concentration

TABLE II
DIURNAL VARIATION OF PBL HEIGHT (M) ON THE DAYS WITH THE NOCTURNAL OZONE MAXIMA EPISODES AND THE FOLLOWING DAY

PBL height (m) on							
UTC(HR)	IST (HR)	19.08.13 -20.08.13	21.08.13-22.08.13	30.09.13 -01.10.13	17.09.14-18.09.14	02.01.15-03.01.15	*09.12.14-10.12.14
0	5:30	474.000	315.4	318.3	0	168.1	1.5
3	8:30	605.200	578.7	443.8	474.3	185.4	114.2
6	11:30	847.600	741.1	876.8	1307.4	383.7	783.2
9	14:30	910.400	816.9	806.8	1484.9	726.5	1124.1
12	17:30	1066	658.5	695.8	695.9	252.5	79.4
15	20:30	865.2	257.2	658.5	77.9	86.9	22.6
18	23:30	747	383.7	429	45.4	22	92
21	2:30	723	381.6	335.4	70	21.5	66
0	5:30	811.4	369.5	334.9	57.1	74.4	43.2
3	8:30	717.5	673	502	352	131.8	117
6	11:30	1056.6	1176.4	950.2	1366.9	511.3	827.1
9	14:30	885.7	1076.6	726.3	1490.1	893.6	1120.2
12	17:30	713.6	630.2	668	177.8	360.6	43.5
15	20:30	660	142	600.3	114.7	116.8	50.5
18	23:30	639.3	137	347.6	125.8	120.6	91
21	2:30	596.6	115.1	261.4	68.5	89	72

^{*} Day with the highest daytime and nighttime ozone concentration

 $TABLE~III\\ DIURNAL~VARIATION~OF~VERTICAL~MIXING~COEFFICIENTS~(KZ)~(m^2/s)~in~ The~Boundary~Layer~on~ The~Days~with~ the~Nocturnal~Ozone~Maxima~Episodes~and~ the~Following~Day$

Vertical mixing coefficient (m²/s) on							
UTC(HR)	IST (HR)	19.08.13 -20.08.13	21.08.13-22.08.13	30.09.13-01.10.13	17.09.14-18.09.14	02.01.14-03.01.14	*09.12.14-10.12.14
0	5:30	28.460	14.140	9.952	0.145	4.346	0.667
3	8:30	44.110	62.740	29.120	13.000	11.480	4.106
6	11:30	50.070	75.380	69.160	14.190	53.200	15.550
9	14:30	64.240	69.070	63.900	11.430	89.780	23.160
12	17:30	63.350	23.470	36.330	1.950	34.800	0.288
15	20:30	76.100	19.570	36.420	2.355	11.210	0.182
18	23:30	97.050	25.490	20.430	2.370	7.958	1.765
0	5:30	95.830	22.990	21.280	0.680	6.083	1.242
3	8:30	60.030	47.360	45.270	10.010	12.230	4.826
6	11:30	111.100	81.080	90.200	12.460	60.510	10.390
9	14:30	79.990	49.690	44.800	31.130	67.680	18.580
12	17:30	46.520	22.590	37.760	25.590	11.200	0.067
15	20:30	55.590	6.378	42.810	11.680	8.404	0.327
18	23:30	63.030	6.127	16.790	8.143	5.425	2.195

^{*} Day with the highest daytime and nighttime ozone concentration

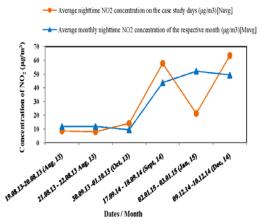
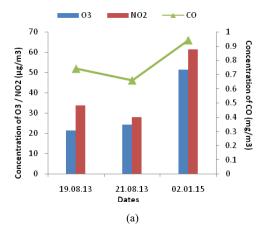
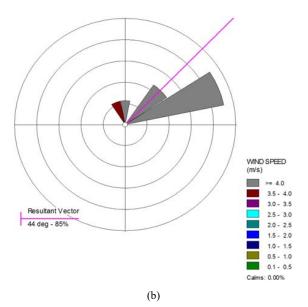


Fig. 3 Comparison of average nighttime concentration of NO_2 during the nocturnal maxima episodes with the average monthly concentration of NO_2





NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 19 Aug 13

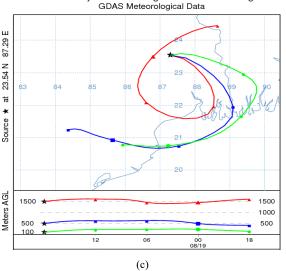


Fig. 4 (a) Concentration of ozone and its precursors (NO₂ and CO) over Kolkata, (b) Wind rose diagram showing the variation of wind speed and wind direction over the urban area during the nighttime of 19.08.13 and (c) Backward trajectories for 19th August, 2013.

The nighttime concentration of NO₂ (Fig. 3) plays a vital role in nocturnal ozone chemistry as shown in (2) and (3).

1. Day 1 (19.08.13)

On 19.08.13, the nighttime ozone concentration ranges from 23.912 - 35.613 $\mu g/m^3$ and the average nighttime ozone concentration (31.523 $\mu g/m^3$) exceeded the average daytime ozone level (28.129 $\mu g/m^3$).

Backward trajectory analysis [Fig. 4 (c)] ending at 1800 UTC (23:30 IST) shows that air mass passes through the polluted areas of Jamshedpur and Kolkata before reaching the destination [Fig. 4 (a)]. Air mass circulation is observed over the region. The concentration of ozone, NO₂, and CO over

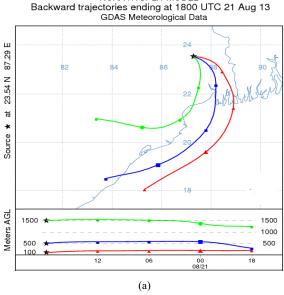
Kolkata is obtained from automatic monitoring station of WBPCB at Victoria Memorial. It is observed that substantial amount of ozone and its precursors (NO2 and CO) are present in the in the atmosphere of the metropolitan city on 19.08.13 [Fig. 4 (a)]. So, the air mass passing through Kolkata might be responsible transporting ozone to the observational site. Moreover, the precursors may also lead to photochemical formation of ozone under suitable conditions during its journey from Kolkata to the chosen site. Presence of limited nighttime NO₂ in the boundary layer (N_{avg}< M_{avg} in Fig. 3) restricts the removal of nocturnal ozone as per (2) and (3). Such condition contributes to the accumulation of surface ozone during nighttime. Similar result of interrupted removal of nocturnal ozone by reactions with NO2 is also reported in Kemaman, Terengganu [6]. Investigation of the characteristics of the PBL height and vertical mixing coefficient (Tables II and III) reveals the scenario of elevated PBL height and enhanced vertical mixing coefficient during the nocturnal period of 19.08.13 - 20.08.13. These boundary layer characteristics lead to better mixing of ozone rich air at higher altitude with the ozone poor layers of lower altitude thereby leading to the increase the nocturnal surface ozone concentration over the site. Therefore, occurrence of high nocturnal ozone may be a manifestation of the combined effect horizontal movement of air mass as well vertical transport.

2. Day 2 (21.08.13)

The nighttime ozone concentration range and average are 22.834 – 38.671 μg/m³ and 31.046 μg/m³, respectively.

The backward trajectory analysis ending at 18:00 UTC [Fig. 5 (a)] at three altitudes (100m, 500m and 1500m) shows that ambient air is a combination of both continental air mass and marine air mass originating from Bay of Bengal. Inspite of absence of any anthropogenic activities, marine environment may have high ozone concentration due to downward transport from the stratosphere [16] and advection from the adjoining landmass [17]. During their residence time over the continental landmass, air masses at 500m and 1500 m got exposed to local pollution and the precursors for the formation of daytime ozone got accumulated in the air mass resulting in the formation of ozone under favorable meteorological conditions. Specifically, air mass at 500m height passed through Kolkata which contains high concentration of ozone, NO₂ and CO [Figs. 5 (a) and 4 (a)] and Gopalpur. A cluster of sponge iron industries is present in Gopalpur which discharge NO₂ and CO in the environment as pollutants. The windrose diagram, Fig. 5 (b), shows that east- southeasterly wind blows over the urban during the nocturnal period of this day. Low level of nighttime NO₂ in the nocturnal boundary layer (N_{avg}< M_{avg} in Fig. 3) leads to interrupted removal reactions [see (2) and (3)] which in turn allowed ozone to remain in the

The values of vertical mixing coefficient (Table III) and PBL height (Table II) suggest favorable conditions for the vertical transport of ozone from higher ozone rich layers to lower ozone deficit layers close to earth's surface.



NOAA HYSPLIT MODEL

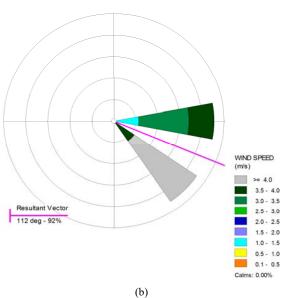


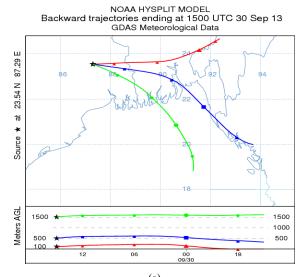
Fig. 5 (a) Backward trajectory analysis for 21st August, 2013 and (b) windrose diagram showing the variation of wind speed and wind direction over the urban area during the nighttime of 21.08.13

3. Day 3 (30.09.13)

On 30.09.13, the nighttime ozone concentration ranges from $13.034-29.733~\mu g/m^3$ and the average nighttime ozone concentration is found to be $22.146~\mu g/m^3$.

Fig. 6 (a) shows that air masses at the altitude of 100 m and 500 m enter the site from the neighboring countries. So, Trans - border source identification and dispersion of pollutants require further investigation. Like Day 2 (21.08.13), ambient air reaching the site at 15:00 UTC is a mixture of continental and marine air masses. So, the air mass originating from Bay of Bengal (at 1500 m) might be responsible for the elevated surface ozone concentration at the observational site during the nocturnal period of 30.09.13 and 01.10.13 [Fig. 6 (a)].

Wind rose diagram [Fig. 6 (b)] also suggests the presence of easterly wind over the urban area during the nocturnal period. Moreover, some unidentified local sources also influences the nocturnal ozone concentration of this area.



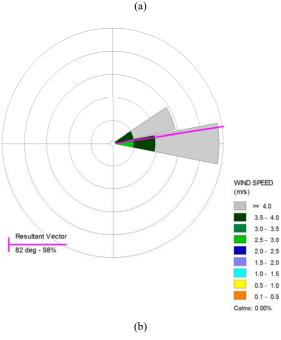


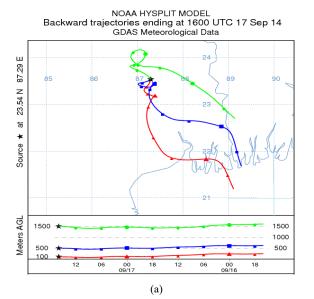
Fig. 6 (a) Backward trajectory analysis for 30th September, 2013 and (b) wind rose diagram showing the variation of wind speed and wind direction over the urban area during the nighttime of 30.09.13

Tables II and III suggest the contribution of vertical transport in enhancing the nocturnal surface ozone level.

4. Day 4 (17.09.14)

The average nocturnal ozone concentration was found to be $88.741 \mu g/m^3$ which is considerably higher than the daytime average of that day $(63.764 \mu g/m^3)$ and the range of ozone

concentration during the nocturnal period was $14.347 - 337.630 \,\mu\text{g/m}^3$.



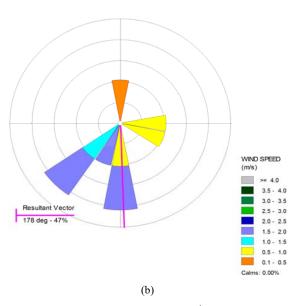


Fig. 7 (a) Backward trajectory analysis for 17th September, 2014 and (b) wind rose diagram showing the variation of wind speed and wind direction over the urban area during the nighttime of 17.09.14

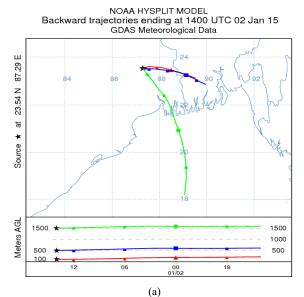
The sudden increase of ozone was found during 20:00-22:00 (IST). Backward trajectory analysis at three different altitudes (100 m, 500 m, and 1500 m) ending at 16:00 UTC (22:00) shows that air mass resides over the continental area and accumulates considerable amount of ozone and its precursors [Fig. 7 (a)]. Air mass at 100 m altitude travels through alloy industries, iron and steel industries, and sponge iron industries in and around Durgapur before reaching the site. Moreover, air mass at 15:00 travels through iron and steel industry of Asansol which might be the reason of incursion of ozone during nighttime. Low speed south – westerly and

southerly wind [Fig. 7 (b)] leads to the accumulation of transported ozone over the urban area during this nocturnal period.

The values of PBL height and vertical mixing coefficient (Tables II and III respectively) suggest very little or no contribution of vertical transport of in abrupt increase of ozone at night time.

5. Day 5 (02.01.15)

The average nighttime ozone concentration was 36.748 $\mu g/m^3$ while the range was found to be 20.678- 46.628 $\mu g/m^3$. The nocturnal ozone maxima occurred between 18:00 h and 22:00 h (IST).



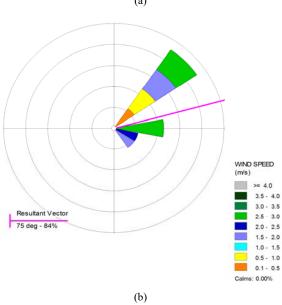
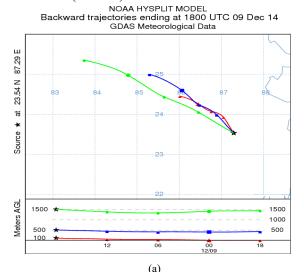


Fig. 8 (a) Backward trajectory analysis for 2nd January, 2015 and (b) wind rose diagram showing the variation of wind speed and wind direction over the urban area during the nighttime of 02.01.15

The backward trajectory analysis ending at 14:00 UTC (19:30 h, IST) shows the arrival of both marine and continental air masses over the observational site. Marine air mass (at 1500m height) travelling through the polluted regions of Kolkata carries substantial amount of ozone and its precursors (NO₂ and CO) [Figs. 8 (a) and 4 (a)]. Like Day 2 (21.08.13), air mass originating in the neighboring country is found to reach the site which requires further investigation and analysis. Limited amount of nighttime NO₂ (Navg > Mavg in Fig. 3) does not favor the ozone removal reactions [see (2) and (3)] thereby contributing to enhanced nocturnal ozone concentration. Boundary layer characteristics given in Tables II and III are not in favor of the vertical transport of ozone.

6. Day with Highest Daytime and Nighttime Ozone Concentration (09.12.14)



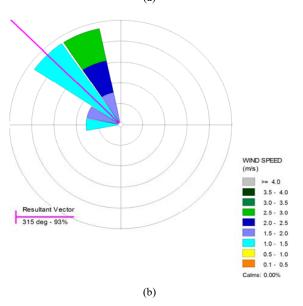


Fig. 9 (a) Backward trajectory analysis for 9th December, 2014 and (b) wind rose diagram showing the variation of wind speed and wind direction over the urban area during the nighttime of 09.12.14

The highest average nighttime ozone concentration during the entire study period of two years was recorded on 09.12.14 (228.210 $\mu g/m^3$). The backward trajectory analysis ending at 18:00 UTC (23:30 h IST) of this day shows the arrival of air masses through the polluted continental landmass [Fig. 9 (a)].

Air mass moves across the polluted regions of Patna where a number of industries (thermal power plant, iron and steel industry etc.) are present. Before entering the study area, the precursors of ozone probably get accumulated in the air mass from iron and steel industry of Asansol which in turn enhances the concentration of ozone during the nighttime. Wind rose diagram [Fig. 9 (b)] further justifies the transport of ozone from polluted regions along with the moderate speed northwesterly wind. Along with horizontal transport and PBL phenomena, meteorology is also found to play a crucial role in the nocturnal ozone level. The meteorological parameters like temperature, humidity, pressure, and wind speed are known to have important roles in formation and transport and dispersion of ozone and its precursors during daytime and nighttime.

It is observed from Fig. 3 that the nighttime concentration of NO_2 does not play significant role in the nocturnal ozone maxima episodes on 30.09.13, 17.09.14, and 09.12.14.

TABLE IV

CORRELATION COEFFICIENTS (R) OF O₃ CONCENTRATION WITH RESPECT TO METEOROLOGICAL PARAMETERS DURING THE OCCASIONS OF HIGH NOCTIFINAL OZONE

Correlation	rioeroidi	Wind		
coefficient(r)	Temperature	Pressure	Humidity	speed
Ozone	-0.398	0.420	-0.654	-0.345

Although temperature is known to be positively correlated with the concentration of ozone during daytime, but reverse trend is observed during nighttime. Photochemical formation of ozone ceases during nighttime, so temperature does not play a significant role at night. It is observed that pressure is positively correlated with nocturnal ozone concentration (Table IV). It is because of the fact that high pressure systems suppress the atmospheric turbulence and favors the accumulation of ozone under the stable nocturnal layer near the surface. Humidity holds inverse relationship with the nighttime ozone concentration. Similar relationships of nocturnal ozone concentration and meteorological parameters were also reported over Kolkata [7]. Table IV shows that the wind speed is negatively correlated with ozone concentration. It is known that lower wind speed restricts the dispersion and dilution of pollutants thereby allowing the accumulation of nighttime ozone near the earth's surface.

IV. CONCLUSION

This study attempts to understand the probable sources of surface ozone during nighttime over a tropical urban area. Five occasions of high nocturnal ozone concentration are analyzed over this urban area. High nighttime ozone level is found to be the manifestation of the combined effects of horizontal transport, vertical transport, concentration of NO₂ and meteorology. The day with the highest daytime as well as nighttime ozone (i.e. 09.12.14) could not be satisfactorily

justified as the boundary layer characteristics of that date are not favorable vertical transport of ozone. Further exploration of role of NO and N_2O_5 as the nighttime ozone sinking agents may help in clear understanding of the sources of high concentration of surface ozone over this urban area.

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