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Study on surface ozone and its precursors at an urban site of Delhi, India

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The measurements of surface ozone (O_3), oxides of nitrogen (NO_x), carbon monooxide (CO), methane (CH_4) and total non-methane hydrocarbons (TNMHCs) have been carried out at an urban site of Delhi, India during 1–31, May 2014 to study the influence of ozone precursors (NO_x, CO, CH_4 and TNMHCs) in the formation of surface O_3 over Delhi. In the present study, the average mixing ratios of surface O_3, NO, NO_2, CO, CH_4 and TNMHCs have been recorded as 37.1 ± 9.8 ppb, 20.4 ± 13.1 ppb, 14.7 ± 3.2 ppb, 1.4 ± 0.5 ppm, 2.6 ± 0.4 ppm and 0.13 ± 0.09 ppm, respectively. The surface O_3, NO, NO_2, CO, CH_4 and TNMHCs have shown significant diurnal variations during study. The result reveals that the mixing ratio of surface O_3 positively correlate with NO_2, TNMHCs, NO_2/NO and NMHCs/NO_x and influence the surface O_3 production at the observational site of Delhi.

Keywords: Ozone, Ozone precursors, Ozone production efficiency

1 Introduction

The ambient air quality is deteriorating day by day due to anthropogenic activites. The emission of toxic trace gases (O_3, NO, NO_2, CO, CH_4 and TNMHCs etc.) in the lower troposphere has been increasing due to the industrialization and globalization during the past decades. The enhancement of mixing ratios of trace gases modulates the Earth's climate because of their efficiency to modify the radiation and energy balance of the earth-atmosphere-system[1]. Surface O_3 is an important trace gas in the lower troposphere which plays a key role in enhancing the oxidizing capacity of the atmosphere and exerts adverse effects on human health as well as damages ecosystem and agricultural crops[2-5]. Ozone is a secondary air pollutant because its formation occurs in the presence of sunlight and its precursors, i.e., NO_x, CO and volatile organic compounds (VOCs), etc., which control the budget of tropospheric ozone[6-7]. Apart from fuelling the formation of tropospheric O_3, a major tropospheric pollutant, the emissions and oxidative products of VOCs significantly influence the chemical composition of the atmosphere. The mixing ratio of O_3 may be directly affected by the changes in photolysis rate constant and indirectly by the NO_x and HO_x budget modifications. As a consequence, NO destroys O_3, forming NO_2 through photolysis. Surface O_3 forms in the presence of sunlight from a chemical reaction between hydrocarbons (VOCs) and nitrogen oxides, both of which are emitted by human activities such as fossil fuel burning as well as by natural sources. The increase of industrial activities, vehicular traffic, and agricultural activities over the last century has resulted in a strong increase of emissions of CO, NO_x, CH_4 and VOCs and these species are involved in the chemical production of ozone in the troposphere[8-10].

The regional features of surface O_3 of different regions are different depending upon the nature of the source and meteorological condition. The mixing ratios of O_3 precursors are increasing rapidly in Southeast Asia as a result of the fast growth of transportation and industrial sectors[11-14]. In tropical countries, biomass burning, especially from forest fires also contributes to ozone in the atmosphere[15,16]. The temporal variations of O_3 have been reported at many sites including rural, urban, coastal and mountain sites of India[11-18]. Different groups[19-29] have conducted extensive studies over India and reported higher O_3 levels during late autumn and winter extending through May. However, role of O_3 precursors *viz.*, VOCs or TNMHCs in the formation

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*Corresponding author (E-mail: sudhir.npl@nic.in) of surface O_3 is limited. In this context present study is more important. In this paper we report the mixing ratios of surface O_3 and its precursor gases (NO, NO_2, CO, CH_4, TNMHCs, etc.) and role of O_3 precursors gases in the formation of surface O_3 during summer season (as an episodic study) at an urban site of Delhi, India.

2 Methodology

The measurements of surface O_3, NO, NO_2, CO and TNMHCs have been carried out at sampling site (28°38′N, 77°10′E; 218 m mean sea level) of CSIR-National Physical Laboratory, New Delhi during 1-31 May, 2014. The sampling site represents a typical urban atmosphere, surrounded by huge roadside traffic and agricultural fields in the southwest direction. This area is under the influence of airmass flow from the northeast to northwest in winter and from southeast to southwest in the summer. In Delhi, the increase in vehicles not only affects the total consumption of fuel but also increases the traffic congestion, vehicles idling time and delay events which ultimately results in more emission of NO_x, hydrocarbons, and CO. The temperature of Delhi varies from minimum (monthly average: 12.9 °C) in winter (November to February) to maximum (monthly average: 34.8 °C) in summer (March to June). The average rainfall in Delhi during monsoon (July to September) is of the order of ~800 mm. The subtropical atmosphere of Delhi and large scale emission of precursor gases cause significant increase in the surface O_3 concentration.

A UV-based Ozone analyzer (Model: 49C; M/s Thermo Environmental Instruments, Massachusetts, USA) was used for measurement of surface O_3. O_3-analyzer was calibrated periodically with primary standard of ozone with an accuracy of < ± 2%. NO and NO_2 were measured using NO_x-Analyzer (Model: CLD 88 p, M/s. ECO Physics AG. Switzerland) using a photocatalytic converter (Model: PLC 860 M/s. ECO Physics AG. Switzerland) with accuracy of ± 0.050 ppb. NO_xanalyzer was calibrated periodically using Zero Air Generator (Model: PAG-003, M/s. ECO Physics AG, Switzerland, accuracy ± 0.01 ppb) and NIST certified NO span gas (500 ppb ± 5%).Carbon monoxide was measured using non-dispersive infrared gas filter correlation analyzer (Model: 48CTL; M/s Thermo Environmental Instruments, Massachusetts, USA). CO-analyzer was calibrated periodically using NIST traceable certified CO gas (10.1 ppm).The mixing ratio of NMHCs and CH_4 were measured using Methane-NMHCs Analyzer (Model 55C, M/s. Thermo Scientific, USA) operating on FID method. These analyzers were operated continuously with uninterrupted power supply during study.

In addition, the meteorological parameters (temperature, RH, wind speed, wind direction and pressure, etc) were measured by using sensors of a meteorological tower (4 stages tower of 30 m height), which is 100m away from the observational site within the same campus. Meteorological tower measures the above mentioned parameters at four different heights (above ground level). We used the meteorological data available at 10 m height to correlate the surface O_3 and its precursors gases. The sampling inlets of all analyzers were also stationed at ~10 m height above ground level.

3 Results and Discussion

The average mixing ratios with standard deviation of surface O_3, NO, NO_2, CO, CH_4 and TNMHCs are summarized in Table 1 whereas time series plots of daily average value of these trace gases are shown in Fig. 1 . The average mixing ratio of surface O_3 ranged from 12.9-96.3 ppb with an average value of 37.1 ± 9.8 ppb during study period. Elevated O_3 mixing ratio observed during the midday (1200-1400 h) throughout the study period. The daytime maximum O_3 mixing ratio may be explained on the basis of large photochemical O_3 production. Photochemical production of O_3 remained strong during the afternoon, mainly from the oxidation of natural and anthropogenic hydrocarbons, CO and CH_4 by hydroxyl (OH) radicals in the presence of sufficient amount of NO_x[30]. The lowest mixing ratio at nighttime was due to in-situ destruction of O_3 by

Table 1 – Average mixing ratios of ambient O_3, NO, NO_2, CO, CH_4 and TNMHCs during study at Delhi

Trace gases	Average	Daytime	Nighttime	Minimum	Maximum
O_3 (ppb)	37.1 ± 9.8	43.0 ± 12.1	31.3 ± 7.5	12.9	96.3
NO (ppb)	20.4 ± 13.1	16.4 ± 9.0	24.4 ± 17.2	0.6	93.4
NO_2 (ppb)	14.7 ± 3.2	14.2 ± 2.6	15.2 ± 3.7	6.2	28.5
CO(ppm)	1.4 ± 0.5	1.3 ± 0.4	1.6 ± 0.5	0.8	2.8
CH_4 (ppm)	2.6 ± 0.4	2.5 ± 0.4	2.6 ± 0.4	2.1	4.3
TNMHC (ppm)	0.22 ± 0.09	0.19 ± 0.04	0.25± 0.14	0.02	0.82

± standard deviation (*n* > 500)

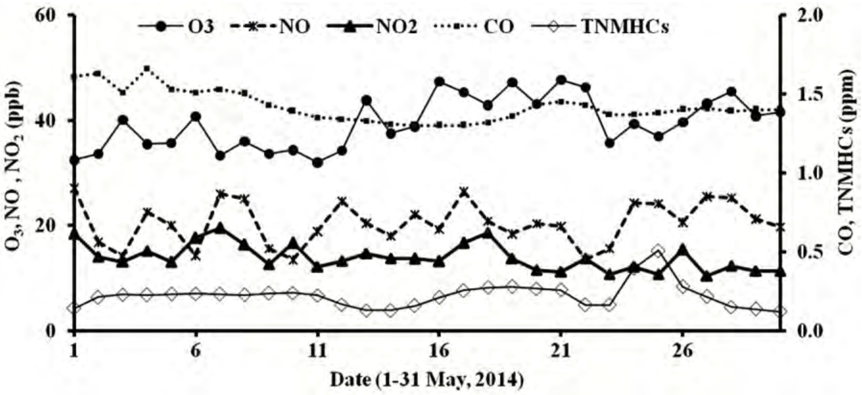

Fig. 1 – Time series plots of daily average value of trace gases (O_3 NO, NO_2, CO and TNMHCs) at Delhi

deposition and/or the reaction between O_3 and NO[31]. Higher variations in the average mixing ratio may be attributed to a sharp increase in the O_3 mixing ratio during the daytime. Jain *et al.*[23] have also reported very high O_3 mixing ratio during the bright sunny days in Delhi. During the monsoon season low mixing ratio of surface O_3 was reocorded which may be due to the reduction of solar radiation during rains and cloudy weather. Nishanth *et al.*[5] reported the minimum (13.8 ± 4.3 ppb) average mixing ratio of surface O_3 at Kannur, India whereas Lal *et al.*[20] reported the maximum (30 ± 3 ppb) average mixing ratio of surface O_3 over Ahmedabad, India.

The average mixing ratio of NO was recorded as 20.4 ± 13.1 ppb with a range of 0.6-93.4 ppb (Table 1). An increase in the atmospheric NO mixing ratio was observed during the early morning and thereafter decreases to a minimum throughout the daytime during study. During evening hours, pollutant emissions from vehicles are trapped in the descending boundary layer[25,32-34]. Daily NO cycle was observed higher during winter which may be due to lower mixing height of atmospheric boundary layer and presence of adequate precursors at the observational site[35]. Ambient NO_2 mixing ratio ranges from 6.2-28.5 ppb with an average value of 14.7 ± 3.2 ppb during the study. Increase in NO_2 mixing ratio during morning may be attributed to the balance between photochemical destruction of NO_2 and chemical reaction of NO with O_3. However, due to photochemical reaction, NO_2 breaks into NO and O^1D, which produces O_3 in the presence of sunlight. During traffic hours, fresh vehicular emission of primary oxidant NO gives an additional peak in the morning. The formation of secondary oxidant NO_2 attains its peak, delayed by a few hours when the balance between the chemical reactions of NO with O_3 and the photochemical destruction of NO_2 reaches maximum[36-37].

The CO mixing ratio ranged from 0.8-2.8 ppm with an average of 1.4 ± 0.5 ppm during study. In the present study, CO mixing ratio was significantly correlated with temperature (r^2= -0.74) and RH (r^2= 0.68). According to photochemical reaction, CO reacts with water vapor, producing OH radical and O^1D in the presence of UV radiation and leads to formation of ozone in the presence of sufficient NO_x. Stable CO concentration between 0700-1000 h may be attributed to an increase in traffic concentration[36,38]. The average mixing ratio of CH_4 and TNMHCs was recorded as 2.6 ± 0.4 and 0.22 ± 0.09 ppm, respectively, with a range of 2.1-4.3 and 0.02-0.82 ppm, respectively (Table 1).

During study higher daytime and lower nighttime mixing ratio of surface O_3 was recorded, whereas the higher mixing ratios for NOx, CO, CH_4 and TNMHCs were observed during nighttime. (Table 1). The variation in O_3 mixing ratio is also influenced by boundary layer processes, regional emission, long range transport and meteorology. The boundary layer height increases after sunrise, reaching a maximum during noontime and descends after sunset. During morning hours, NO and NO_2 (NO_x) mixing ratio started to increase due to the emission from the vehicles and their reactions to produce O_3. During evening hours, pollutant emissions from vehicles get trapped in the descending boundary layer[33]. Due to lower boundary layer height, the mixing ratio of pollutants near the surface increases. Non-significant day and nighttime variation in mixing ratio of ambient CO was also observed during study. During daytime, in the presence of UV radiation, CO reacts with water vapor producing OH radical and O^1D and leads to the formation of surface O_3 in the presence of sufficient

NO_x. The non-significant diurnal variation in mixing ratios of ambient CH_4 and TNMHC was also observed at the observational site of Delhi (Table 1). In polluted environments like Delhi, the photo-oxidation of TNMHCs in the presence of NO_x leads to the formation of O_3. The importance of TNMHCs as O_3 precursor depends largely on their reactivities and ambient mixing ratios. The major urban sources of TNMHCs are from vehicle exhaust, chemical industries and refinery operations, etc.[35].

Figures 2-4 shows the correlation (at $p \leq 0.05$) between mixing ratio of O_3 vs. NO; O_3 vs. NO_2; O_3 vs. NO_2/NO; O_3 vs. TNMHCs; O_3 vs. TNMHCs/NO_x and CH_4 vs. TNMHCs; during study period in Delhi. In the present study, the mixing ratios of surface O_3 and NO were non-significantly anti-correlated (r^2 = -0.41), whereas mixing ratios of surface O_3 and NO_2 were non-significantly positively correlated (r^2 = 0.19) during study (Fig. 2). Similarly, the mixing ratio of O_3 and NO_2/NO was also significantly positively correlated (r^2 = 0.53) during summer (Fig. 3). O_3 production during daytime is driven by

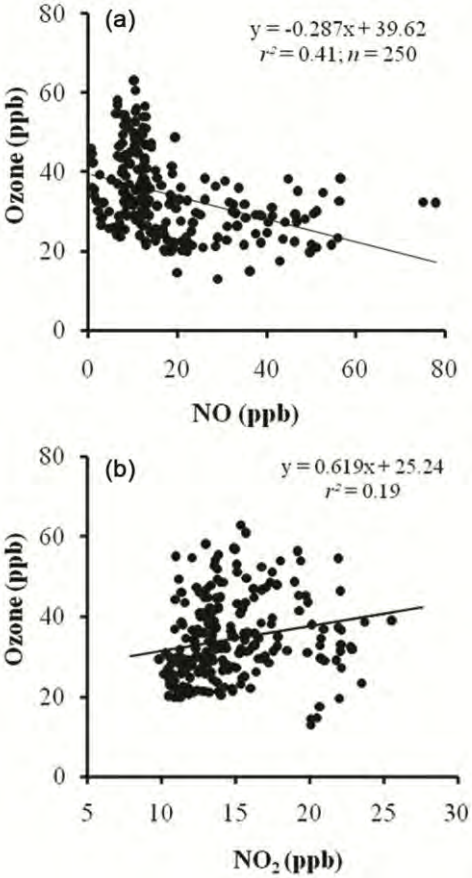

Fig. 2 – Scatter plots showing the correlation between (a) O_3 and NO (b) O_3 and NO_2 at Delhi

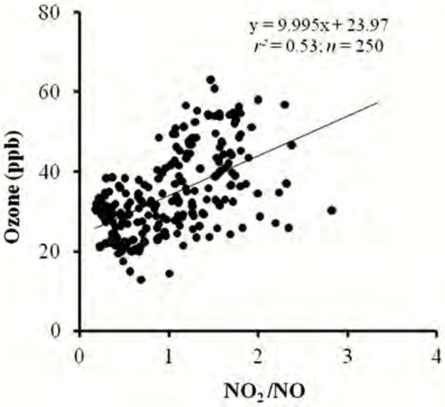

Fig. 3 – Variation of mixing ratio of O_3 with NO_2/NO at Delhi

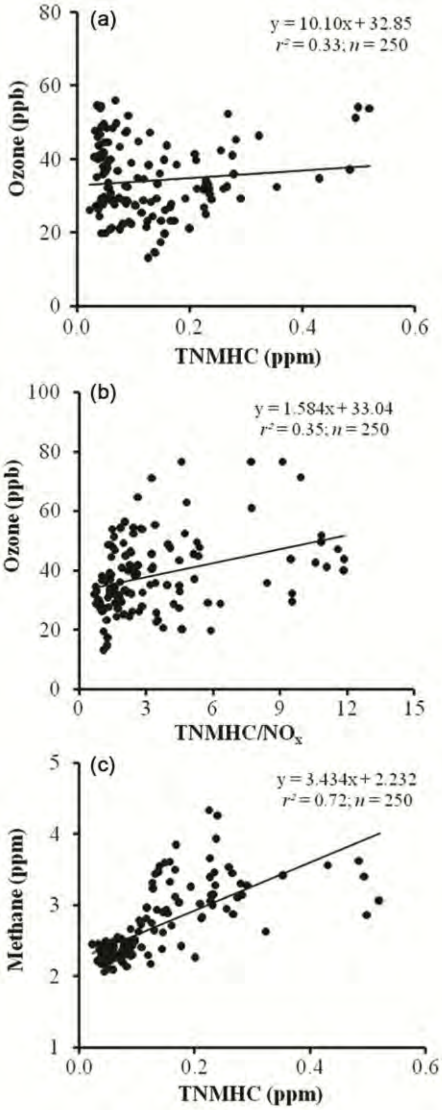

Fig. 4 – Scatter plots showing the correlation between (a) O_3 and TNMHC (b) O_3 and TNMHC/NO_x (c) CH_4 and TNMHCs at Delhi

the photochemical reaction between hydroxyl radicals, organic peroxy radicals and NO, while it is removed at night by dry deposition and destruction by alkenes and NO. The O_3 and NO_x mixing ratios show an inverse relationship due to titration of O_3 during daytime. Non-significant correlation of O_3 vs. TNMHCs; O_3 vs. TNMHCs/NO_x also indicates the influence in the formation of surface O_3 at the observational site. The mixing ratio of surface O_3 was also calculated using (equation, $[O_3] = j[NO_2] \times [NO_2]/ k_3[NO]$ where, $k_3 = 1.8\times10^{-14}$ cm^3 mol^{-1} s^{-1}; and $j[NO_2] = k_1 = 2.07\times10^{-2}$ cm^3 s^{-1}; dependent on temperature and solar insolation) NO_x as a precursor gases and shown in Fig. 5 alongwith their correlation. Sander *et al.*[39] reported that ($[O_3] = j_{10}$ $[NO_2]$ / $k_{13}[NO]$) the $[O_3]$ is directly proportional to $[NO_2]$ / $[NO]$ ratio. In the present study the average $[NO_2]$ / $[NO]$ was recorded as 1.10. The mixing ratio of NO and NO_2 was measured in Delhi by Sharma *et al.*[36] for different seasons and they reported that $[NO_2]$ / $[NO]$ ratio 0.93 in winter and 1.08 in summer. It is well documented that $[NO_2]$ / $[NO]$ ratio (concentration of NO_2 and NO) does not remain constant throughout the year however, changed with seasons. Therefore, seasonal change in $[NO_2]$ / $[NO]$ ratio, which leads to the seasonal change in O_3 mixing ratio is due to the NO-NO_2 chemistry. The result shows that the formation of surface O_3 as urban site of Delhi is complex process and depends on so many factors including ozone precurcurs. However, O_3 precursors play an inportant role in the formation of surface O_3 at urban site of Delhi.

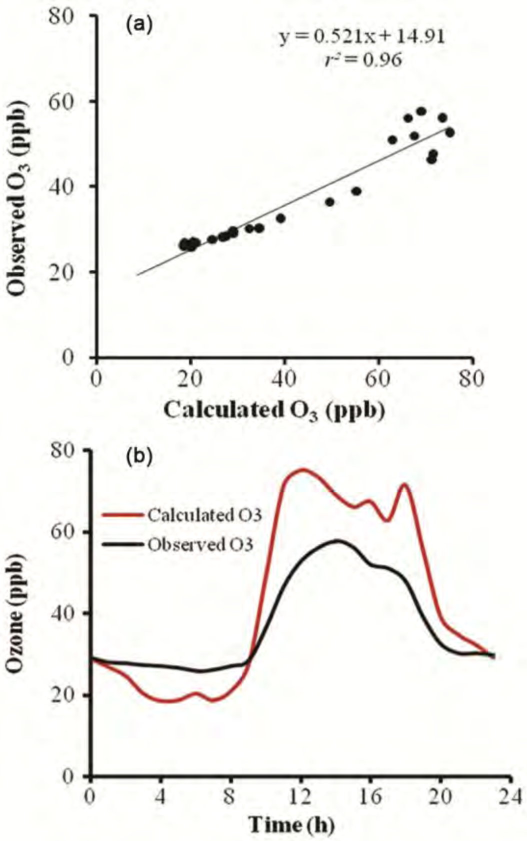

Fig. 5 – Scatter plots between (a) observed O_3 and calculated O_3 (b) diurnal variation of observed and calculated O_3

4 Conclusions

In the present study, the average mixing ratios of surface O_3, NO, NO_2, CO, CH_4 and NMHC were recorded as 37.1 ± 9.8 ppb, 20.4 ± 13.1 ppb, 14.7 ± 3.2 ppb, 1.4 ± 0.5 ppm, 2.6 ± 0.4 ppm and 0.13 ± 0.09 ppm, respectively, over Delhi as an episodic study. Surface O_3, NO, and NO_2 showed prominent diurnal variation during study, whereas the mixing ratios of CO, CH_4 and NMHCs showed non-significant diurnal variation. The study demonstrated that the O_3 precursor gases (NO, NO_2, CO, CH_4 and TNMHCs) influence the magnitude of O_3 at Delhi. However, long-term measurements of O_3 and its precursors will lead to better understanding of seasonality of these pollutants.

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