Original research article

Influence of ozone precursors and particulate matter on the variation of surface ozone at an urban site of Delhi, India

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ABSTRACT

Continuous measurements of surface O_3 and its precursors (NO, NO_2, CO, CH_4 and NMHCs) at an urban site of Delhi, India during January 2012 to December 2013 are presented. In the present study, the annual average mixing ratios of surface O_3, NO, NO_2, CO, CH_4 and NMHC were 30 ± 6 ppb, 24 ± 6 ppb, 15 ± 4 ppb, 1.5 ± 0.4 ppm, 2.4 ± 0.4 ppm and 0.4 ± 0.1 ppm, respectively. The maximum average mixing ratios of surface O_3, NO and NO_2 were observed during the summer, whereas, the minimum average mixing ratios of ambient NO and NO_2 were during monsoon seasons. The surface O_3, NO and NO_2 have shown the prominent diurnal variations during all the seasons at the observational site of Delhi. The result reveals that the surface O_3 was negatively correlated with NO_x and CO during the study. The linear scatter plot analysis shows that the $PM_{2.5}$ and PM_{10} present in the ambient air of Delhi influence the production of surface O_3 at observational site.

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1. Introduction

The emission of trace gases (O_3, NO, NO_2, CO, SO_2, CH_4 and NMHCs etc.) in the lower troposphere has been increasing due to the industrialization and globalization during the past decades. The enhancement of mixing ratios of these 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 O_3 [3]. Apart from fueling 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, the 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 [6–8].

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 [9–12]. In tropical countries, biomass burning, especially from forest fires also contributes to ozone in the atmosphere [13,14]. The temporal variations of O_3 have been reported at many sites including rural, urban coastal and mountain sites of India [9–14]. Different groups [15–21] have conducted extensive studies over India and reported higher O_3 levels during late autumn and winter extending through May. Recently, the Indian Space Research Organization has initiated a network program in India to retrieve the Chemistry, Transport and Modeling of trace species at various locations in the Indian sub-continent and various groups have been involved in the long-term measurements of surface O_3 and precursors; these results are quite promising [22–28].

Particulate matter has complex effects on solar actinic flux photolysis rates in the troposphere and the surface O_3. The

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reduction in surface O_3 production indicates the different impacts between absorbing and non-absorbing aerosols on photolysis frequencies. The ambient aerosol can reduce the photolysis frequencies of $J [O_3 (^1D)]$ and $J [NO_2]$ in the planetary boundary layer and it can reduce ground level O_3 concentration. This reduction could be due to the aggregate structure of aerosol particles, which provides a large specific surface area for heterogeneous interactions with reactive trace gases such as surface O_3 [5]. Many studies have focused on the efficiency of aerosols that can modify the photolysis rate of trace gases and revealed that absorbing aerosols can diminish UV actinic flux throughout the troposphere, leading to a reduction in near-surface ozone production [29–31]. Meteorology plays an important role in air pollutants formation, dispersion, transport and dilution. Therefore, the variations in local meteorological conditions, such as wind speed, wind direction, temperature and relative humidity (RH), can affect the temporal variation of surface O_3 and its precursors [5].

This paper studies the seasonal and diurnal variations of surface O_3 and its precursor gases (NO_x, CO, CH_4, etc.) and meteorological effects at an urban site of Delhi, India. The impact of particulate matter ($PM_{2.5}$ and PM_{10}) in the reduction of surface O_3 at sampling location of Delhi is also studied.

2. Materials and methods

2.1. Description of site

The measurements of surface O_3, NO, NO_2 and CO 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 January 2012 to December 2013, whereas NMHCs and CH_4 have been measured during May to October 2012. The sampling site represents a typical urban atmosphere, surrounded by huge roadside traffic and agricultural fields in the southwest direction (Fig. 1). This area is under the influence of air mass flow from the northeast to northwest in winter and from southeast to southwest in the summer. Roadside vehicles, industrial emission and biomass burning, etc. could be the major sources of carbonaceous aerosols and several other pollutants [32]. The combination of factors including industries, power plants, domestic combustion of coal and biomass, and transport is contributing to air pollution [21,32]. 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 [1]. 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 October) is of the order of ~825 mm. Monthly variation of ambient temperature, RH, wind direction and wind speed at the observational site during study are given in Fig. 2. The subtropical atmosphere of Delhi and large scale emission of precursor gases cause significant increase in the surface O_3 concentration. Sufficient build up of tropospheric ozone has been reported with wide temporal and seasonal variation [15,19,21].

2.2. Experimental set up

A UV-based Ozone analyzer (Model: TECO-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_x-analyzer 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 (8.1 ppm). The mixing ratio of NMHCs and CH_4 were measured using Methane-NMHC Analyzer (Model 55C, M/s. Thermo Scientific, USA) operating on FID method. These analyzers were operated continuously (15–20 d in each month) with uninterrupted power supply for the period of January 2012 to December 2013.

PM_{10} and $PM_{2.5}$ samples ($n = 60$ each) were collected simultaneously on Whatman quartz microfiber (QM-A) filters by using Fine Particle Sampler (APM 550, Make: M/s. Envirotech, India; one unit for PM_{10} and another unit for $PM_{2.5}$). Ambient air was passed through a quartz filter (47 mm) at a flow rate of 1 m^3 h^{-1} (accuracy ± 2%) for 24 h during the sampling period. The amount of PM_{10} and $PM_{2.5}$ (in μg m^{-3}) calculated on the basis of the difference between final and initial weights of the quartz filters measured by a micro balance (M/s. Mettler-Toledo, resolution: ± 10 μg) was determined by dividing the amount of total volume passed during the sampling.

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 100 m away from the observational site within the same campus. Meteorological tower measures the above mentioned parameters at four different heights (above ground level, i.e., agl). The various sensors are placed in the tower at different levels of 1.5, 10, 20 and 30 m agl height from the surface. We use the meteorological data available at 10 m height to correlate the surface O_3 and its precursors during the study period. Sampling inlets of all analyzers were stationed at ~10 m height agl. We have also analyzed the difference of the ambient temperature between different levels [(2 and 3: 10–20 m agl), (3 and 4: 20–30 m agl) and the height between them are 10 m] to estimate the atmospheric stability of the observational layer.

Fig. 3 shows the averaged diurnal difference in temperature (°C m^{-1}) between different layers during winter, summer and monsoon seasons of the study period. During winter, at the observational site the average temperature at 10, 20 and 30 m agl were 11.90, 12.69 and 12.83 °C, respectively. The average difference of the ambient temperature between 10–20 and 20–30 m agl were 0.079 °C m^{-1} (range: −0.08–0.27 °C m^{-1}) and 0.014 °C m^{-1} (range: −0.03–0.05 °C m^{-1}), respectively during winter season. The average ambient temperature at 10, 20 and 30 m agl were 30.20, 31.30 and 31.53 °C, respectively during summer season whereas, the average difference of the ambient temperature between 10–20 and 20–30 m agl were 0.109 °C m^{-1} (range: −0.06–0.28 °C m^{-1}) and 0.024 (range: −0.02–0.06 °C m^{-1}), respectively. During monsoon, the average difference of the ambient temperature between 10–20 and 20–30 m agl ranged from −0.49 to 0.26 and 0.01 to 0.06 °C m^{-1}, respectively with average value of −0.114 (at 10–20 m agl) and 0.036 °C m^{-1} (20–30 m agl). During the study period temperature variation between 10 and 20 m agl were higher than the 20–30 m agl. However, the analysis shows that the temperature variation were < 0.3 °C bewteen the levels upto 30 m agl and stable during the study period and not influence the sampling height of surface O_3 and its precursors gases.

3. Results and discussion

3.1. Mixing ratios of surface O_3 and its precursors

The average seasonal variation in mixing ratios of surface O_3, NO, NO_2, CO, CH_4 and NMHCs with an annual average values are

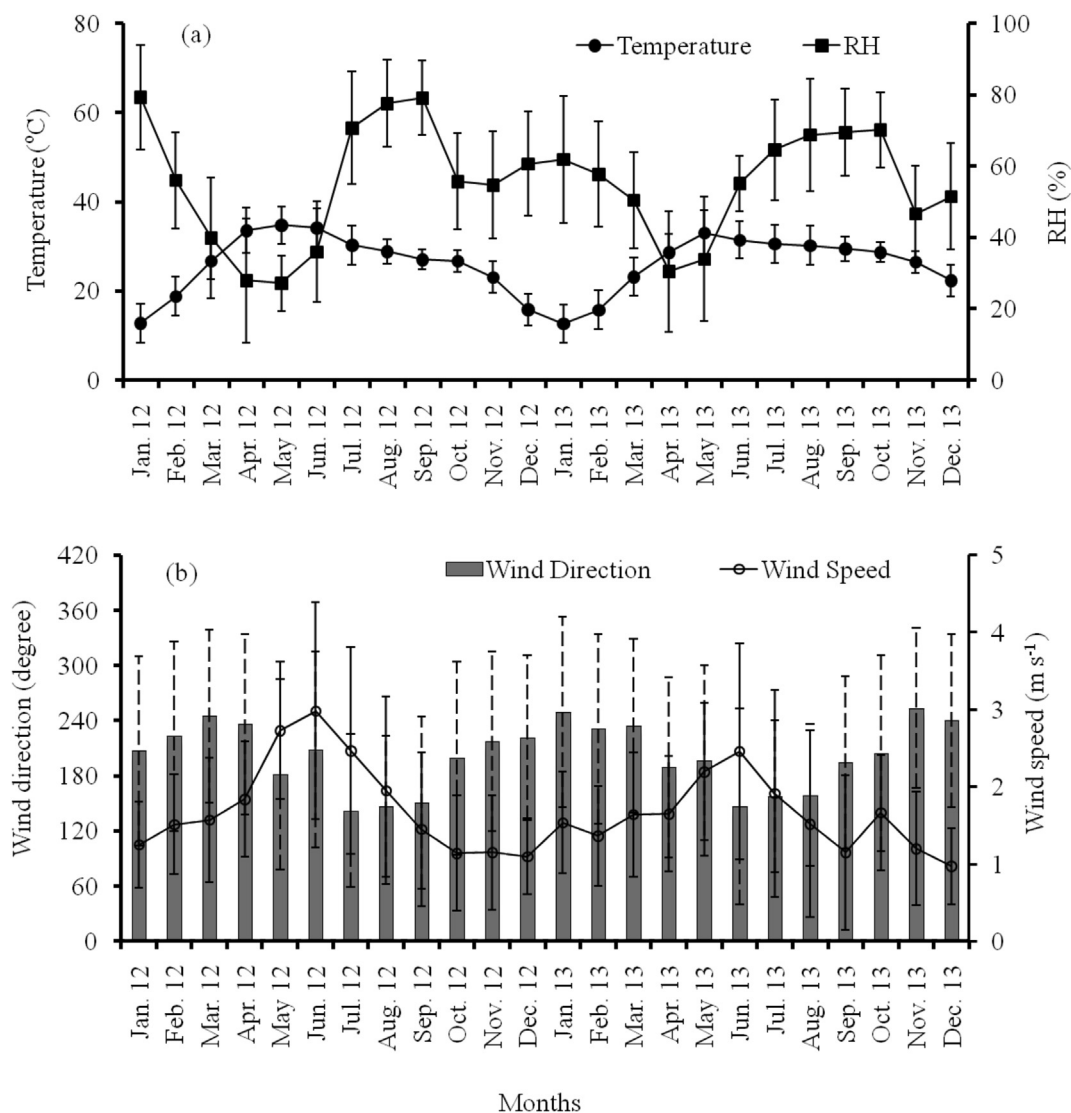**Fig. 1.** Map of sampling location.

Fig. 2. Monthly average variations in (a) temperature and RH; (b) wind direction and wind speed at Delhi during 2012–2013.

summarized in Table 1. The annual average mixing ratio of surface O_3 ranged from 4 to 86 ppb with an average value of 30 ± 6 ppb. The monthly variations in mixing ratios of surface O_3, NO, NO_2 and CO were also recorded during the study period (Fig. S1, in supplementary information). During winter, the average mixing ratio of surface O_3 was recorded as 29 ± 6 ppb with maxima (38 ± 7 ppb) in daytime (0600–1800 h) and minima (20 ± 4 ppb) at nighttime (1800–0600 h, absence of sunlight). The mixing ratio of surface O_3 was ranging from 5–102 and 4–71 ppb during summer and monsoon seasons respectively, with an average value of 34 ± 7 and 28 ± 6 ppb, respectively. Among the seasons the highest average mixing ratio of surface O_3 was recorded during summer, followed by winter and monsoon seasons (Table 1). Elevated O_3 mixing ratio observed during the midday (1200–1400 h) throughout the study period (Fig. 4). 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 [33]. The lowest concentration at nighttime was due to in situ destruction of O_3 by

deposition and/or the reaction between O_3 and NO [34]. 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. [19] 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 recorded may be due to the reduction of solar radiation during rains and cloudy weather. Table S1 (in supplementary information) shows the comparison of average mixing ratio of surface O_3 at various locations of Delhi and other part of India with present study. The comparative study reveals that the average mixing ratio of surface O_3 varying from 24 to 41 ppb over Delhi (Table S1, in supplementary information). Nishanth et al. [5] reported the minimum (13 ± 3 ppb) average mixing ratio of surface O_3 at Kannur, India whereas Lal et al. [16] reported the maximum (13 ± 3 ppb) average mixing ratio of surface O_3 over Nainital, India.

The annual average mixing ratio of NO was recorded as 24 ± 6 ppb with a range of 2–60 ppb during the study (Table 1). The average NO mixing ratio was recorded higher during summer (27 ± 6 ppb) followed by winter (23 ± 7 ppb) and monsoon seasons (20 ± 4 ppb) (Table 1). An increase in the atmospheric NO mixing
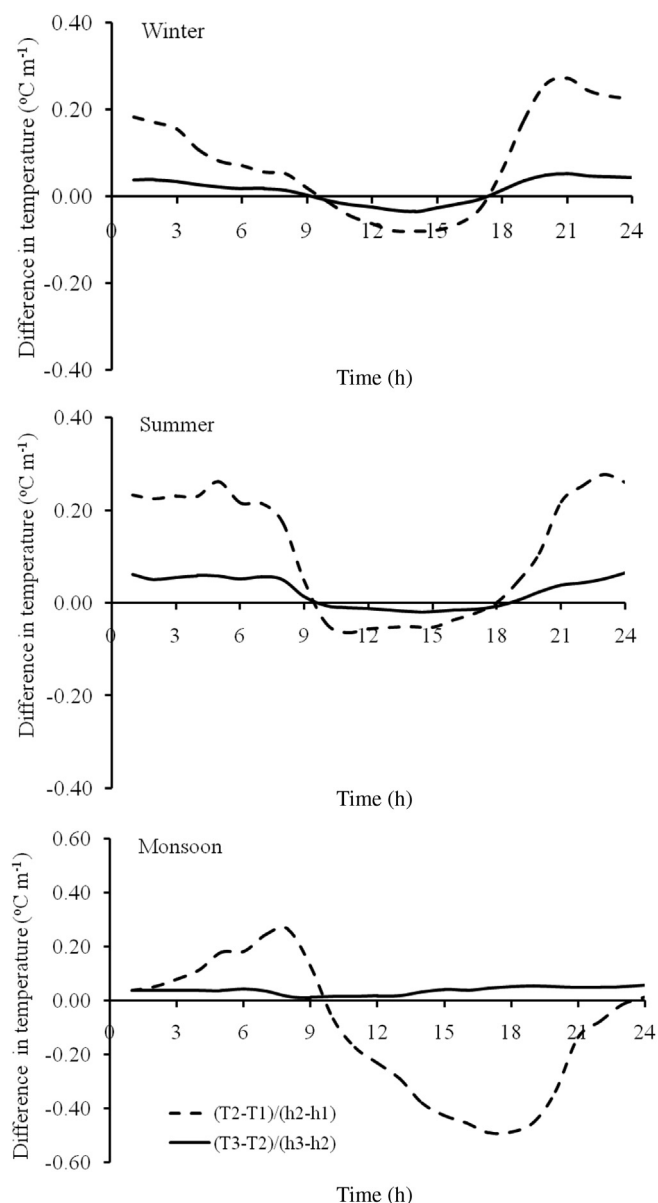
Fig. 3. Difference in average (diurnal) temperature between 10 and 20 m height ($h_2-h_1 = 10$ m) and 20–30 m height ($h_3-h_2 = 10$ m) from the surface during winter, summer and monsoon seasons.

ratio was observed during the early morning and thereafter decreases to a minimum throughout the daytime (Fig. 4) at all the seasons. During evening hours, pollutant emissions from vehicles are trapped in the descending boundary layer [11,21]. Daily NO cycle was observed higher during winter may be due to lower mixing height of atmospheric boundary layer and presence of adequate precursons at the observational site [35].

Ambient NO_2 mixing ratio ranges from 1 to 39 ppb with an average value of 14 ± 4 ppb during the study. The average NO_2 mixing ratio was recorded higher during summer (19 ± 6 ppb) followed by winter (14 ± 3 ppb) and monsoon seasons (10 ± 3 ppb) (Table 1). Increase in NO_2 mixing ratio (Fig. 4) around 0600–0900 h during the all seasons 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. After sunset, conversion of NO to NO_2 due to chemical interaction with O_3 dominates when photochemical conversion of NO_2 to NO stops because of absence of sunlight.

The CO mixing ratio ranged from 0.7 to 2.9 ppm with an average of 1.5 ± 0.4 ppm during study. The CO mixing ratio was recorded higher during winter (1.7 ± 0.5 ppm) followed by monsoon (1.4 ± 0.5 ppm) and summer (1.3 ± 0.4 ppm) seasons (Table 1). In the present study, CO mixing ratio was significantly correlated ($r^2 = -0.83$; at $P < 0.05$) with temperature and RH ($r^2 = 0.74$ at $P < 0.05$). 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 and 1000 h may be attributed to an increase in traffic concentration.

The average mixing ratio of CH_4 and NMHCs were recorded as 2.4 ± 0.4 and 0.4 ± 0.1 ppm, respectively, with a range of 0.5–2.8 and 0.1–0.8 ppm, respectively. During summer, the average mixing ratio of CH_4 was recorded as 2.5 ± 0.2 ppm, whereas the average mixing ratio of CH_4 was 2.4 ± 0.5 ppm during monsoon season (Table 1). Non-significant seasonal variation in the mixing ratio of CH_4 and NMHC was observed during the study period.

3.2. Diurnal variations of surface O_3 and its precursors

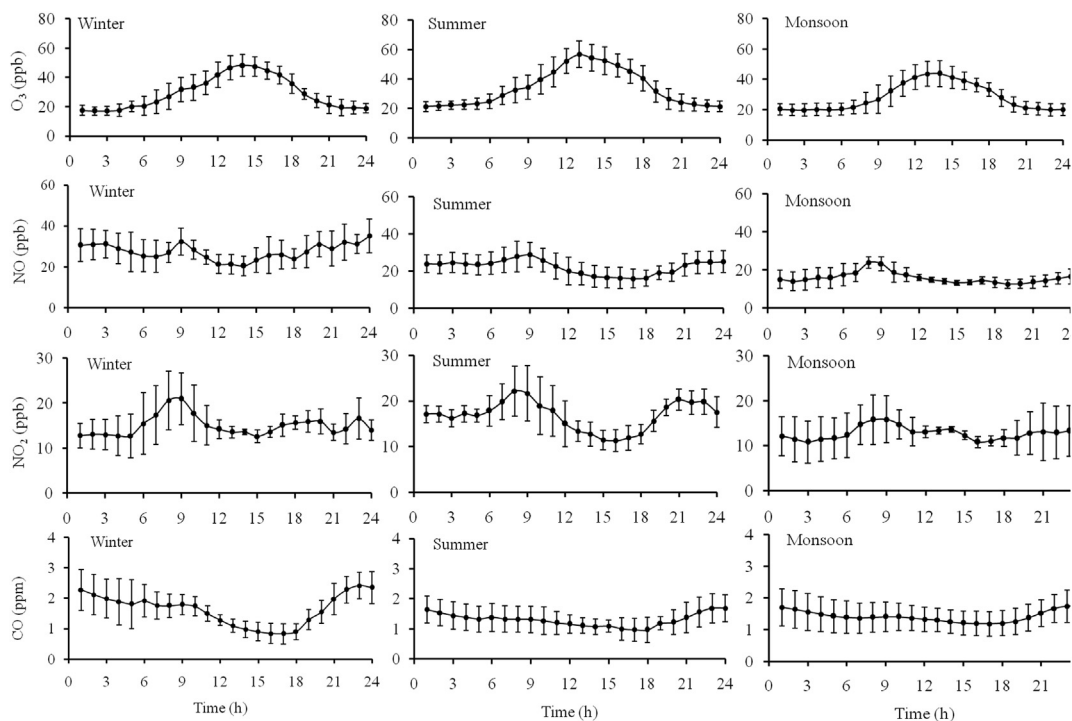Fig. 4 shows the average diurnal variation of surface O_3, NO, NO_2 and CO at Delhi during winter, summer and monsoon seasons. Among the seasons higher daytime and higher nighttime mixing ratio of surface O_3 was recorded during the summer, whereas the minimum averaged daytime/nighttime mixing ratio of surface O_3 was recorded during winter (Table 1). In the present study, significant diurnal variation of surface O_3 was observed during winter, summer and monsoon seasons (Fig. 4). 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 winter the daytime and night time average mixing ratio of NO was recorded as 20 ± 4 and 27 ± 7 ppb, respectively. Whereas, the daytime and nighttime average mixing ratio of ambient NO was recorded as 25 ± 7 and 28 ± 6 ppb, respectively during summer season. A significant diurnal variation of ambient mixing ratio of NO was observed during all seasons (Fig. 4). The day and nighttime variation in the mixing ratio of ambient NO_2 was also observed during winter, summer and monsoon seasons (Table 1). During morning hours, NO and NO_2 (NO_x) mixing ratio started to increase due to the emission of hydrocarbons from the vehicles and their reactions to produce O_3. During evening hours, pollutant emissions from vehicles get trapped in the descending boundary layer [35]. During winter season the convective activities and turbulent mixing were weak, which leads to lower boundary height. Due to lower boundary layer height, the mixing ratio of pollutants near the surface increases. In addition, biomass burning during winter season, causing transport of NO, NO_2, CO, and NMHCs to this site [35,36].

The nighttime mixing ratio of ambient CO (2.1 ± 0.6 ppm) was recorded significantly higher than daytime mixing ratio of CO (1.4 ± 0.4 ppm) during winter season (Fig. 4). Non-significant day and nighttime variation in mixing ratio of ambient CO was also observed during summer and monsoon seasons. During daytime, in the presence of UV radiation, CO reacts with water vapor producing

Table 1
Average mixing ratios of ambient O_3, NO, NO_2, CO, CH_4 and NMHCs during winter, summer and monsoon seasons at Delhi.

Trace gases	Average	Daytime (0600–1800 h)	Nighttime (1800–0600 h)	Minimum	Maximum
Surface O_3 (ppb)					
Winter	29 ± 6	38 ± 8	20 ± 4	3	77
Summer	34 ± 7	44 ± 9	24 ± 5	5	102
Monsoon	28 ± 6	35 ± 7	21 ± 4	4	77
Annual	30 ± 6	37 ± 8	22 ± 4	4	86
NO (ppb)					
Winter	23 ± 7	30 ± 5	27 ± 7	3	57
Summer	27 ± 6	25 ± 7	28 ± 6	1	71
Monsoon	20 ± 4	19 ± 3	22 ± 3	2	52
Annual	24 ± 6	21 ± 5	26 ± 5	2	60
NO_2 (ppb)					
Winter	14 ± 3	16 ± 3	13 ± 3	1	41
Summer	19 ± 6	15 ± 4	24 ± 4	2	45
Monsoon	10 ± 3	10 ± 2	11 ± 3	1	28
Annual	15 ± 4	13 ± 3	16 ± 3	1	39
CO (ppm)					
Winter	1.7 ± 0.5	1.4 ± 0.4	2.1 ± 0.6	0.6	4.2
Summer	1.3 ± 0.3	1.1 ± 0.3	1.5 ± 0.4	0.5	3.9
Monsoon	1.4 ± 0.4	1.3 ± 0.4	1.5 ± 0.5	0.9	3.8
Annual	1.5 ± 0.4	1.3 ± 0.4	1.8 ± 0.5	0.7	2.9
CH_4 (ppm)					
Winter	–	–	–	–	–
Summer	2.5 ± 0.2	2.4 ± 0.2	2.6 ± 0.3	0.6	2.9
Monsoon	2.3 ± 0.4	2.3 ± 0.3	2.5 ± 0.4	0.4	2.7
Annual	2.4 ± 0.3	2.5 ± 0.2	2.5 ± 0.3	0.5	2.8
NMHC (ppm)					
Winter	–	–	–	–	–
Summer	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.1	0.7
Monsoon	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.1	0.7
Annual	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.1	0.7

± standard deviation ($n > 5000$).

Fig. 4. Average diurnal variations of surface O_3, NO, NO_2, and CO winter, summer and monsoon seasons.

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 NMHC was also observed at the observational site of Delhi during the summer and monsoon seasons in 2012 (Table 1). In a polluted environments like Delhi, the photo-oxidation of NMHCs in the presence of NO_x leads to the

Table 2
Observed rate of change of O_3 (ppb h^{-1}) at Delhi and at sites of India.

Sites	Rate of change at (0800−1100 h) ppb h^{-1}	Rate of change at (1700−1900 h) ppb h^{-1}	References
Delhi	4.7	−5.5	Present study
Delhi	4.5	−5.3	[38]
Pune	4.8	−2.6	[37]
Ahmedabad	5.9	−6.4	[16]
Thumba	4.8	−2.6	[17]
Gadanki	4.6	−2.6	[17]
Anantpur	4.6	−2.5	[22]
Dayalbag	2.2	−2.3	[24]
Pantnagar	5.6	−8.5	[26]
Mohal	7.3	−5.9	[28]
Kannur	4.9	−6.4	[12]

Table 3
Correlation matrix of O_3 with NO, NO_2, CO, $PM_{2.5}$ and PM_{10} during winter, summer and monsoon seasons.

Parameters	Winter	Summer	Monsoon
O_3 versus NO	−0.431	−0.138	−0.427
O_3 versus NO_2	0.237	0.224	0.283
O_3 versus CO	−0.597*	−0.477*	−0.460
O_3 versus $PM_{2.5}$	−0.761*	−0.672*	−0.599*
O_3 versus PM_{10}	−0.647*	−0.583*	−0.676*

*Significant at $P < 0.05$.

formation of O_3. The importance of NMHCs as O_3 precursor depends largely on their reactivities and ambient mixing ratios. The major urban sources of NMHCs are from vehicle exhaust, chemical industries and refinery operations, etc. [37]. Seasonal variation of NMHC is mainly influenced by the photochemical removal, source strengths, dilution due to atmospheric mixing of air parcels and transport from the source regions of the observational site.

3.3. Rate of change of surface O_3

The average rates of change of ozone (d(O_3)/dt) during morning hours (0800−1100 h) and in the evening hours (1700−1900 h) at Delhi was estimated as 4.7 and −5.6 ppb h^{-1}, respectively (Table 2). The averaged diurnal rates of change of surface O_3 during winter, summer and monsoon was also observed at the observational site (Fig. S2, in supplementary information). The rates of change of surface O_3 was recorded as 5.5 ppb h^{-1} during morning and −5.3 ppb h^{-1} during evening hours at Delhi [38]. The average rates of change of O_3 during morning and evening hours at various locations of India are summarized in Table 2. At Mohal, a hilly area the average rate of change of O_3 in morning was 7.3 ppb h^{-1} which may be considered higher due to fast production of O_3 by freshly emitted precursors [28]. At urban locations like Ahmedabad, Pantnagar and Delhi, the average rate of change of O_3 during evening hours is more than the morning hours. This is because of high production of NO_x from vehicular emission and also due to fast titration of O_3 in the evening at these experimental sites [17,39].

3.4. Interaction of O_3 precursors on surface O_3

Table 3 shows the correlation matrix between mixing ratio of O_3 and NO; O_3 and NO_2; and O_3 and CO during winter, summer and monsoon seasons in Delhi. In the present study, the mixing ratios of surface O_3 and NO were non-significantly anti-correlated during winter ($r^2 = -0.431$ at $P < 0.05$), summer ($r^2 = -0.138$) and monsoon ($r^2 = -0.427$) seasons. Whereas mixing ratios of surface O_3 and NO_2 were non-significantly positively correlated during winter ($r^2 = 0.237$), summer ($r^2 = 0.224$) and monsoon ($r^2 = 0.283$)

seasons (Table 3). Similarly, the seasonal variations of mixing ratios of CO and O_3 were also anti-correlated during winter ($r^2 = -0.597$), summer ($r^2 = -0.477$) and monsoon ($r^2 = -0.460$) seasons (Table 3). O_3 production during daytime is driven by 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.

The concentrations of $PM_{2.5}$ and PM_{10} present in the ambient air of Delhi are correlated with the mixing ratio of surface O_3 to explore the influence of $PM_{2.5}$ and PM_{10} on surface O_3 (Table 3). Particulate matter has complex effects on solar actinic flux photolysis rates in the troposphere and at the surface. The reduction in surface O_3 production indicates the different impacts between absorbing and non-absorbing aerosols on photolysis frequencies. The atmospheric PM can reduce the photolysis frequencies of J $[O_3 (^1D)]$ and J $[NO_2]$ in the planetary boundary and it can reduce ground level O_3 concentration. This reduction could be due to the aggregate structure of aerosol particles, which provides a large specific surface area for heterogeneous interactions with reactive trace gases such as O_3. A negative correlation was observed for daily mean values of $PM_{2.5}$ and PM_{10} with O_3 during the winter, summer and monsoon seasons. Surface O_3 shows significant negative correlation with $PM_{2.5}$ and PM_{10} concentrations during winter, summer and monsoon (Table 3). Surface O_3 sink into aerosol is a significant part of its destruction process and is characteristics of cold period.

4. Conclusions

In the present study, the annual average mixing ratios of surface O_3, NO, NO_2, CO, CH_4 and NMHC were 30 ± 6 ppb, 24 ± 6 ppb, 15 ± 4 ppb, 1.5 ± 0.4 ppm, 2.4 ± 0.4 ppm and 0.4 ± 0.1 ppm, respectively over Delhi. During summer the average mixing ratios of surface O_3, NO and NO_2 recorded highest, whereas, the minimum average mixing ratios of ambient NO and NO_2 observed during monsoon season. Surface O_3, NO, and NO_2 showed prominent diurnal variation during all the seasons, whereas the mixing ratios of CO, CH_4 and NMHCs showed non-significant diurnal variation. The study demonstrate the O_3 precursor gases (NO, NO_2, and CO) influencing the magnitude of O_3 at Delhi. The result also reveals that the particulate matter present in the ambient air of Delhi has close links to surface O_3 mixing ratio.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.serj.2015.10.001.

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