Study of surface ozone (O_3) and its relationship with NO , NO_2 , NO_x , OX and CO at five different locations in New Delhi, India from 2013 to 2019

Priyanka Sinha

India Meteorological Department

Siddhartha Singh (✉ siddhartha.singh74@gmail.com)

India Meteorological Department <https://orcid.org/0000-0002-2259-8790>

Pooja Saroj

India Meteorological Department

Gufran Beig

Indian Institute of Tropical Meteorology

B. S. Murthy

Indian Institute of Tropical Meteorology

Research

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Abstract

In the present study, continuous measurements of Surface Ozone (O_3), Oxides of Nitrogen (NO_x ($NO + NO_2$)), and carbon monoxide (CO), monitored at five different locations in Delhi National Capital Region have been studied for the period 2013–2019. The five monitoring locations used are namely IMD Lodi Road, IGI Airport Palam, CV Raman Dheerpur, CRRI Mathura Road, and NCMRWF Noida. The average hourly concentration of O_3 , NO, NO_2 , CO, NO_x ($NO + NO_2$), and $OX(NO_2 + O_3)$ are found in the range of 32.44 ppb to 36.57 ppb, 19.46 to 28.09 ppb, 20.83 to 26.89 ppb, 1.67 to 1.89 ppm, 43.04 to 54.99 ppb, and 54.06 to 60.99 ppb respectively during the study period. Diurnal variation of NO_x and CO Concentrations show higher values during the morning (0600-0900h) and late evening (1900-2400h) hours while the highest concentrations of ozone have been observed during afternoon hours. The relationship between NO, NO_2 , and surface O_3 as a function of NO_x has also been examined during daylight hours (0500hrs IST to 1900 hrs IST) and chemical coupling of the three species i.e. NO, NO_2 and O_3 have been studied. The ground-level concentration of Ozone have been found to decrease with increasing NO_x concentration during daytime. The variations in concentrations of oxidants ($NO_2 + O_3$) with the concentration of $[NO_x]$ have been studied to examine the contributing pollution sources of oxidants at all the study sites. The average rate of change of O_3 concentrations (dO_3/dt) has been examined at all five locations. The monthly and diurnal variation of oxidants $[OX]$ at all the study locations has shown a strong positive correlation with temperature whereas a negative correlation with humidity.

1. Introduction

Atmospheric trace gases are one of the challenging environmental issues in urban and industrial areas in India. It has demanded an increased awareness among the research communities as greenhouse gases and trace gases both alter the energy balance of the climate system. For example, the radiative forcing for the tropospheric ozone (O_3) changes due to the emission of O_3 precursors (e.g. oxides of nitrogen, NO_x , and carbon monoxide, CO) and has been found between $+0.25$ to $+0.65 \text{ W m}^{-2}$ (with a mean value of $+0.35 \text{ W m}^{-2}$). [1]

Tropospheric O_3 has two main sources, namely stratosphere intrusion affecting surface O_3 [2, 3] and in-situ production via photochemical oxidation of carbon-link compounds (i.e. CO, CH_4 , and VOCs), in the presence of NO_x . [3, 4] Ozone production efficiency has been observed to depend on meteorological conditions such as solar radiation flux, wind speed, temperature and pressure. The daytime increase in ozone concentration is a pronounced feature of urban polluted sites, which is basically due to photo-oxidation of the precursor gases such as CO, CH_4 , NMHCs, etc. in the presence of sufficient amounts of NO_x . [5] It has been found that photochemical ozone production in urban areas is more sensitive to NO_x emissions and is less sensitive to VOC emissions. [7] In areas having moderate air pollution, ozone sensitivity to the emission of nitrogen oxides depends on the meteorological conditions and the emission rates of nitrogen oxides. [6] Due to the chemical coupling of ozone and nitrogen oxides, any resultant reduction in the level of nitrogen dioxide is invariably accompanied by an increase in the air concentration

of ozone. It has become important to understand the chemical pathways leading to the formation of ozone in the atmosphere to devise effective strategies to reduce surface ozone levels.

NO_x plays a major role in the oxidizing capacity of the lower atmosphere due to its significant effects on the partitioning, formation and loss of free radical species (OH, HO₂ and RO₂). [7, 8] CO also plays an important role in controlling the oxidizing capacity of the troposphere, by acting as a sink for a larger fraction of reactive hydroxyl (OH) radicals available in the lower atmosphere. [9] The oxidation begins with the reaction of Carbon monoxide (CO) released from various sources present in the lower troposphere with the hydroxyl radical ([•]OH), which is abundantly present near the surface of the earth. The radical intermediate formed by this reaction reacts rapidly with oxygen to give a peroxy radical HO₂[•]. Peroxy radicals then go on to react with NO to give NO₂ which undergoes photolysis to give atomic oxygen and through reaction with oxygen (O₂) a molecule of ozone is produced in the lower troposphere.

India with a population of 1210 million [10] is a developing country with a very fast growing economy. The last decade (2001–2011) showed a compound annual growth rate in the number of registered vehicles of around 10%. [11] As per the Census Report [10], the decadal growth rate of the population of Delhi during 2001–2011 was recorded at 21.2 %. The total number of motor vehicles on road in NCT of Delhi as of 31st March 2018 was 109.86 lakh, showing a 5.81 percent growth from the previous year.[11] The number of vehicles per thousand in the population increased considerably from 317 in 2005-06 to 598 in 2017-18. [11] High ozone levels have been regularly reported from major cities [12–15], with the capital city of New Delhi being the worst affected. [16–18] Surface ozone (O₃) concentrations in New Delhi frequently exceed the national ambient air quality standards prescribed by the Central Pollution Control Board (CPCB), exposing a large population to health-related risks. [19] In lieu of the above, ambient data of NO, NO₂, NO_x, and surface O₃ from five different sites in Delhi have been analyzed for the study period from 2013 to 2019. The relationships between the ambient concentrations of NO, NO₂, and O₃ as a function of NO_x (NO + NO₂) have been studied. In addition, the concentrations of total oxidants [OX], the sum of NO₂ and O₃, and their relationship with NO_x are also studied to understand the sources of OX.

2. Materials And Methods

Delhi is geographically located in the Northern part of India within the latitude 28°24'17" to 28°53'00"N, and longitude 77°45'30" to 77°21'30"E which is a subtropical belt. The summers in Delhi are very hot and winters are very cold. The temperature range varies from 3°C in the winter season to 45°C in the summer season. The winters are marked by mist and fog in the mornings and often sun is seen in the afternoons. The cold wave from the Himalayan region makes winters very chilly. Figure 1 shows the variation of monthly average temperature and relative humidity over Delhi (5 sites average). In this part of India, the dry summer season runs from late March to June, the monsoon season from late June to September, the autumn season/post-monsoon season from October to November and the winter season from December to February. In the monsoon season, the southwest monsoon prevails over India, and precipitation,

occasionally heavy rainfall and high humidity are common throughout the country. After mid-September, the shift of the southwest monsoon to the northeast monsoon generally occurs, which brings air masses from the north and northeast. The dry season can subsequently be classified into two periods, the months of strong solar radiation from April to June and another from October to November.

The System of Air Quality Forecast and Research (SAFAR), a project initiated by the Ministry of Earth Sciences (MoES), New Delhi, India in 2010, has a network of many air quality monitoring stations (AQMS's) and automatic weather stations (AWS) located in and around Delhi and NCR covering an area of 2500 km². Under this project, synchronous measurements of trace gases, viz. surface O₃, NO_x and CO for the period 2013–2019 over New Delhi were carried out using O₃ analyzer (49i; Thermo Scientific, USA, precision ~ 1 ppbv), NO_x analyzer (42i; Thermo Scientific, USA, precision ~ 0.4 ppbv) and CO analyzer (CO11m Environment S. A. France, precision limit ~ 0.1ppmv). O₃ analyzer works on the principle that O₃ molecules absorb ultraviolet (UV) light at a wavelength of 254 nm. NO_x analyzer operates on the principle that NO and O₃ react to produce a characteristic luminescence with intensity proportional to the NO concentration. Calibration of the O₃ analyzer was done on every alternate day using an inbuilt O₃ calibrator, whereas NO_x calibration was performed with a multipoint calibration technique. Carbon monoxide measurements using a CO11m analyzer are based on the technique of the correlation wheel. It operates on the principle of infrared absorption at a 4.67 μm vibration-rotation band of CO. This instrument is regularly calibrated as and when changes in the calibration factors beyond the limits are noticed. The data can be recorded for intervals ranging from 1 min to 24 h with the help of data acquisition systems. In the present case, one-hour data storage is selected. Meteorological parameters e.g. ambient air temperature, wind speed, wind direction and relative humidity, recorded by Automatic Weather Stations (AWS), have been used in the present study.

In this work, we have used continuous air quality and meteorological observation monitored at five locations spread in different directions in Delhi which have been considered as representatives of Delhi (Fig. 2). The five monitoring stations used in this study are CV Raman ITI Institute, Dheerpur (an urban populated site, located in North Delhi); Central Road Research Institute (CRRI), Mathura Road (a heavy traffic site, located in South East Delhi); National Centre for Medium Range Weather Forecasting (NCMRWF), Noida (the heavily loaded polluted site from nearby sources, located in East Delhi), India Meteorological Department (IMD), Lodi Road Site (a cleaner site, located in Central Delhi) and IGI airport Terminal 3 (major airport of the city, located in South West Delhi with heavy traffic all through the day) (Fig. 2).

3. Results And Discussion

.1 Diurnal and Monthly variation of O₃, NO, NO₂, NO_x, OX and CO:

The hourly averaged concentrations of O₃, NO, NO₂, NO_x, OX and CO at all the five study locations i.e. IMD Lodi Road, IGI Airport Palam, NCMRWF Noida, CRRI Mathura road and CV Raman Dheerpur from 2013 to 2019 are shown in Fig. 3. Mean hourly values of concentrations of different parameters along with

standard deviation, maximum and minimum values at all the sites are given in Table 1. During the study period, the hourly averaged concentration of surface O_3 , NO, NO_2 , CO, NO_x ($NO + NO_2$) and $OX(NO_2 + O_3)$ for all five locations have been found in the range from 32.44 ppb to 36.57 ppb, 19.46 to 28.09 ppb, 20.83 to 26.89 ppb, 1.67 to 1.89 ppm, 43.04 to 54.99 ppb and 54.06 to 60.99 ppb respectively. Typically, the concentration of surface O_3 starts increasing gradually after sunrise (between 0630-0700h) attains a maximum around noontime (between 1300- 1500h), and starts declining after this peak. (Fig. 3) The high concentration between 13:00h and 15:00h implies photochemical production of surface O_3 and transport of photochemical build-up of surface O_3 to the measuring site. [20] The decrease in night-time O_3 concentrations is mainly due to titration of O_3 by surface emission of NO and ground-level destruction of O_3 in a shallow boundary layer. The dry deposition directly onto the earth's surface can significantly reduce the level of O_3 . In highly polluted regions, where the level of NO is high, the loss of O_3 may occur due to the following titration reaction:

Table 1
Hourly maximum, minimum, and average values of NO, NO₂, NO_x, O₃, and OX during 2013–2019.

STATIONS	(ppb)	NO	NO ₂	O ₃	NO _x (NO + NO ₂)	OX(NO ₂ + O ₃)	CO(ppm)
IMD LODI ROAD	Average	26.05 ± 13.4	20.83 ± 7.5	33.22 ± 15.08	46.88 ± 17.4	54.06 ± 15.9	1.91 ± 0.5
	Minimum	7.83	10.84	14.11	19.62	30.25	0.87
	Maximum	58.77	39.67	70.37	98.12	85.89	3.10
IGI AIRPORT PALAM	Average	20.0 ± 10	23.44 ± 9.7	32.47 ± 11.7	43.45 ± 19.6	55.91 ± 13.07	1.74 ± 0.8
	Minimum	10.40	7.73	14.71	19.62	33.39	0.85
	Maximum	50.13	41.84	62.56	82.86	96.92	2.90
CV RAMAN DHEERPUR	Average	19.46 ± 7.4	23.58 ± 8.3	36.55 ± 9.19.2	43.04 ± 14.9	60.13 ± 11.6	1.72 ± 0.6
	Minimum	9.36	11.61	22.01	23.19	41.53	0.96
	Maximum	36.38	36.84	59.15	70.33	84.88	3.22
CRR I MATHURA ROAD	Average	28.09 ± 15.38	26.89 ± 9.7	34.09 ± 8.79	54.99 ± 22.7	60.99 ± 13.69	1.67 ± 0.41
	Minimum	10.84	13.06	17.53	25.18	31.12	0.84
	Maximum	57.83	43.12	52.97	100.95	87.30	2.76
NCMRWF NOIDA	Average	20.58 ± 6.5	21.3 ± 7.14	33.28 ± 8.73	41.88 ± 10.64	54.58 ± 12.5	1.83 ± 0.63
	Minimum	8.70	10.57	19.06	24.37	32.22	0.76
	Maximum	36.09	36.42	59.11	58.13	85.99	3.20
*± Standard Deviation

Both NO_x and CO have shown build-up during the morning (0700–0900 h) and late evening/night hours (1900–2400 h) during the study period which is different from the variations in ozone (Fig. 3). Higher levels of NO_x and CO during morning and late evening hours at all the sites used in this study are due to the combinations of anthropogenic emissions, boundary layer processes, chemistry as well as local surface wind patterns. During night hours, the boundary layer descends and remains low till early

morning, thereby resisting the mixing of the anthropogenic emissions with the upper layer. Hence, pollutants get trapped due to shallow nocturnal boundary layer depth resisting the mixing of local emissions with the free tropospheric air. It is important to note that the major anthropogenic source for CO and NO_x in an urban region like New Delhi (mainly NO) is fossil fuel burning (combustion in motor vehicles).[21] Fig. 4 shows the monthly variation of NO, NO₂, O₃, and CO at all the monitoring stations during the study period. The concentrations of NO_x have been found highest in post-monsoon months (October, November and December) and the lowest value in monsoon months (July, August and September). The concentrations of CO have been found highest in winter months (December, January and February) and lowest value in monsoon months (July, August and September) (Table 2 and Table 3). This seasonal pattern may be due to a combined effect of large near-surface anthropogenic emissions, boundary layer processes, retarded photochemical loss owing to lower solar intensity, as well as local surface wind patterns. In contrast, O₃ peaked during the summer months (March, April, May and June) (Fig. 4, Table 2 and Table 3), clearly due to its direct linear relationship with incoming solar radiation.

Table 2
Monthly average Concentrations of NO, NO₂, O₃ and CO in Delhi.

Monthly Average				
Months	NO	NO ₂	O ₃	CO
January	25.53	20.16	25.91	2.07
February	19.42	20.67	29.64	1.81
March	21.92	25.50	33.50	1.95
April	23.89	23.86	39.80	1.81
May	22.56	26.58	41.53	1.71
June	20.47	24.37	40.24	1.56
July	20.06	23.05	35.16	1.81
August	21.74	22.19	28.68	1.52
September	19.86	22.48	31.91	1.35
October	23.13	23.25	38.70	1.76
November	27.75	22.99	33.52	2.08
December	28.73	26.84	31.47	1.87
New Delhi(5 Station avg*)				

Table 3
Average seasonal variation of NO, NO₂, NO_x, O₃ and CO in Delhi.

Seasons	NO	NO ₂	NO _x	O ₃	CO
Winter Season	24.56	22.56	47.12	29.01	1.92
Summer Season	22.21	25.08	47.29	38.77	1.76
Monsoon Season	20.55	22.57	43.13	31.92	1.56
Post Monsoon Season	26.54	24.36	50.90	34.57	1.90

The high solar radiation intensity (i.e. temperature) has a direct influence on chemical kinetic rates and the mechanism pathways for the O₃ production. [22] The photooxidation of CO, CH₄ and NMHCs in presence of a sufficient amount of NO_x and sunlight during the summer months (March-June) leads to the formation of O₃. The concentrations of O₃ showed the highest values in the summer season and the lowest value in the winter season (Table 3). O₃ concentrations were comparable to those reported at other urban locations in India, [18, 21, 23–26) and higher compared to rural and high altitude sites in India. [27, 28]

.2 Variation in rate of change of Surface O₃ at the Urban site:

Figure 5 shows the variation of hourly averaged rate of change of O₃ concentrations (d [O₃]/dt) at all the five sites used in this study during the study period. The rate of change of O₃ can be used as an indicator of urban and rural chemical environments. [29] Urban environments commonly show similar morning and evening rates of change in O₃, while rural sites are characterized by asymmetric diurnal patterns i.e. higher build-up rates in the morning and lower loss rates in the evening hours.[29] This can be because, in morning time O₃ formation is strongly dependent on the available amount of precursors emitted from morning vehicular traffic (0700-1100h) and sudden change in boundary layer height with the sunrise, while the evening time loss rate (1700-2200h) largely depends on nitrous oxide (NO) (conversion of NO₂ to NO in the evening) concentration which participates in O₃ titration processes Eq. (1). The average rates of change of ozone (d [O₃]/dt) during morning hours (0800h-1100h) and in the evening and late evening hours (1700-1900h) at Delhi (5 station average in our study) have been estimated at 4.16 ppbh⁻¹ and – 4.48 ppbh⁻¹, respectively (Table 4). The mean rate of change of O₃ at all the sites used in the present study was found similar to that of other urban locations like Agra, Kanpur, Ahmedabad, Pune and also at an urban site in New Delhi India. [15, 30–34]The night-time rate of change was found almost steady and slightly negative, perhaps due to O₃ loss to surface deposition and also due to fast titration of O₃ in the evening at these experimental sites.

Table 4
Observed rate of change of Surface Ozone (dO_3/dt) in different cities of India.

Site	Type of Site	Rate of change of O ₃ (ppb/h)		References
		(0800h-1100h)	(1700-1900h)	
Delhi*	Urban	4.2	-4.48	(This study)*
Delhi	Urban	4.7	-5.5	[33]
Delhi	Urban	4.5	-5.3	[32]
Kanpur	Urban	3.3	-2.6	[30]
Agra	Urban	2.5	-2.4	[15]
Ahmedabad	Urban	5.9	-6.4	[31]
Pune	Urban	4.8	-2.6	[34]
Anantapur	Rural	4.6	-2.5	[27]
Gadanki	Rural	4.6	-2.6	[29]
Thumba	Coastal (rural)	5.5	-1.4	[35]
Kannur	Coastal (rural)	4.9	-6.4	[36]
Dayalbagh	Rural	2.2	-2.3	[15]
Pantnagar	Hilly	5.6	-8.5	[37]
Mohal	Hilly	7.3	-5.9	[38]
* 5 station avg.				

3.3 Chemical coupling of O₃ and its precursors:

Leighton [39] has demonstrated the fact that in the troposphere the photochemical inter-conversion of O₃, NO and NO₂ is generally controlled by the following reactions:

Where M (usually N₂ or O₂) represents a molecule that absorbs the excess vibrational energy and thereby stabilizes the O₃ molecule formed, $h\nu$ represents the energy of a photon (with wavelength $\lambda = 424 \text{ nm}$)

and O^* is the active mono-atomic oxygen. The above reactions constitute a reversible cycle i.e. the overall effect of Eqs. (2) and (3) are exactly opposite and canceled by the effect of Eq. 4. It represents a null cycle where there is no net production of O_3 . [40, 41] Therefore, these reactions as described in Leighton [40] represents a closed energy system in which oxides of nitrogen (NO_x) is partitioned between its constituents, NO and NO_2 (primary NO_2), and oxidant (OX) is partitioned between its constituents NO_2 and O_3 . This state is also defined as a photo stationary state (PSS). During daylight hours (as these reactions are driven by sunlight) NO, NO_2 and O_3 are at an equilibrium state for a few minutes. [40, 41] Hence the concentrations of the above species during PSS can be defined by the following equation: [39]

$$\frac{[NO][O_3]}{[NO_2]} = \frac{j_1}{k_3} \quad \text{Eq. (5)}$$

Where j_1 is the NO_2 photolysis rate and k_3 is the rate coefficient for the reaction between NO and O_3 , according to Eq. (4). j_1 depends on the intensity of solar radiation. Rate coefficient k_3 for Eq. (4) is temperature-dependent. [55–57] It can be computed using the following equation: [42]

$$k_3 \text{ (ppm}^{-1} \text{ min}^{-1}\text{)} = 3.23 \times 10^3 \exp \left(\frac{-1430}{T} \right) \quad \text{Eq. (6)}$$

Figure 6 shows the diurnally averaged values of rate constant k_3 ($\text{ppm}^{-1} \text{ min}^{-1}$) with an ambient air temperature of IMD Lodi Road station for the year 2019. As discussed earlier, k_3 is directly proportional to temperature; therefore the maximum value of k_3 coincides with the value of ambient air temperature ($^{\circ}\text{C}$) during the noon period. The values of k_3 rise after 0700 h in the morning as the sun rises, and attains its maximum value of $27.37 \text{ ppm}^{-1} \text{ min}^{-1}$ at around 1400 h when the ambient air temperature is maximum, i.e. 26.74°C . The rate of photolysis j_1 for IMD Lodi Road station is calculated using the value of obtained rate constant k_3 and the hourly averaged concentrations (in ppm) of NO, NO_2 , and O_3 . The value was calculated in the range of 0.58 min^{-1} to 1.87 min^{-1} with an average value of 1.02 min^{-1} . Figure 7 describes the relationship between O_3 , NO, NO_2 with NO_x as described in the Eqs. (3) and (4). The figure shows the variations in the daylight (the period of sunlight) concentrations of NO, NO_2 and O_3 versus NO_x . The daylight concentrations were determined using the sunrise and sunset values obtained from the US astronomical site (http://aa.usno.navy.mil/data/docs/RS_OneDay.php), which generally varied between 0500–1900h during summers and 0630–1800h during winters. [40, 41] Polynomial fit curves for NO, NO_2 and O_3 were drawn that adequately described the interaction between the three species.

1. As seen in Fig. 7, it can be observed that surface O_3 concentrations decrease with increasing NO_x concentrations while NO and NO_2 concentrations increase with increasing NO_x concentrations for all the stations used in this study.
2. [NO] concentrations dominate as compared to [NO_2] and [O_3] concentrations at higher values of [NO_x] whereas at lower values of [NO_x], [O_3] dominates over [NO] and [NO_2] for all the sites as can be seen in Fig. 7. [O_3] and [NO] curves cross over with [NO_x] at values ranging between 75.77 ppb to

78.89 ppb, maximum being for CRRM Mathura Road station. This can be due to higher precursor gases concentrations as this is a heavily polluted area as described in the above section. (Sect. 2). When $[\text{NO}_x]$ increases $[\text{O}_3]$ values diminish but values of $[\text{NO}]$ increase as can be seen in Fig. 7 for all the sites.

3. $[\text{NO}_2]$ and $[\text{O}_3]$ curves intersect with $[\text{NO}_x]$ at values ranging between 83.067 to 85.97 ppb, maximum being for CRRM Mathura Road station as can be observed in Fig. 7. When $[\text{NO}_x]$ is < 85.97 ppb $[\text{O}_3]$ is in dominant form.

Figure 7 clearly describes the chemical coupling of the three species as well the interaction and relationship of O_3 with its precursors. The above figure establishes the fact that at higher concentrations of NO_x , O_3 is destroyed and NO_2 remains the predominant form of the oxidant $[\text{OX}]$. Similar behavior has been reported earlier by Clapp and Jenkin [43] and Mazzeo et al. [40] for urban and rural sites in the UK and Buenos Aires, respectively. Similar behavior has also been reported by Tiwari et al. [41] for an urban site in New Delhi, India

Figure 8 presents the variation in daytime O_3 concentration (1-hour average) as a function of the NO_2/NO ratio (sample interval: 1 hour) at all sites during the whole study period. The daylight concentrations were determined using the sunrise and sunset values obtained from the US astronomical site (http://aa.usno.navy.mil/data/docs/RS_OneDay.php) which generally varied between 0500–1900h during summers and 0630–1800h during winters. [40, 41] It was observed that for all the sites, the ambient level of hourly averaged O_3 increases with an increase in the ratio of $[\text{NO}_2]/[\text{NO}]$. According to Fig. 8, concentrations of hourly averaged ambient O_3 at all the 5 sites, increase rapidly at small values of $[\text{NO}_2]/[\text{NO}]$, this may be implicated that when O_3 was at low levels, the reactions of production of O_3 was a dominated reaction. When O_3 concentration reached about 35.98 ppb (5 site average), it became relatively stable. This shows that at an average value of 35.98 ppb, O_3 concentration is close to reaching a photo stationary state. Similar behavior was reported by Han et al. [44] for Tianjin in China.

3.3.1 Relationship between $[\text{NO}_2]$ and $[\text{NO}_x]$

Figure 9 presents the variation of the $[\text{NO}_2]/[\text{NO}_x]$ ratio at all the locations for the whole study period (averaging time: 60 min) in the function of $[\text{NO}_x]$. It has been observed that the $[\text{NO}_2]/[\text{NO}_x]$ ratio decreases with the increase of the $[\text{NO}_x]$ levels. According to the data available, it has been calculated that for New Delhi (5 station average) when $[\text{NO}_x] = 100$ ppb, $[\text{NO}_2]/[\text{NO}_x]$ ratio was found to be ≈ 0.296 . It has been observed that mean $[\text{NO}_2]$ concentrations for all the locations used in the study were not very high (≈ 23.24 ppb). In these cases, the average $[\text{NO}_2]/[\text{NO}_x]$ ratio for New Delhi (5 station average) was calculated to be ≈ 0.51 , which is significantly higher than the ratio generally found in vehicular NO_x emissions. The highest observed values of $[\text{NO}_2]/[\text{NO}_x]$ ratio at all the locations of our study for the whole study period can be explained by an additional oxidation process for NO to NO_2 , possibly that of the reaction of NO with oxygen to form NO_2 : [40, 43]

3.4 Relationship between [OX] and [NOx], [NOx] dependent and [NOx] independent contribution to [OX]

Figure 10 depicts the relationship between daylight averaged (60 min average) concentrations of [OX] with respect to [NOx] at all sites during the whole study period. It is seen from the figure that the concentrations of [OX] increase with the increasing concentration of [NOx] at all the sites of this study. As seen from Fig. 10, at all the sites the curve fits the linear regression curve $[y = mx + c]$. A non-significant positive correlation has been observed at all the sites during the study period (r^2 value ranges between 0.08 to 0.16 at $P = 0.05$). With help of the slope of the curve obtained for all sites, we can divide it into an [NOx] independent contribution and [NOx] dependent contribution for the concentration of oxidants at all the sites of an urban location.[40, 41, 43] The NOx-dependent contribution can be contributed to local contribution sources of oxidants and can also be correlated to primary pollutant sources. [40, 41, 43] It is called as [NOx] dependant contribution because an increase/decrease in [NOx] affects the concentration of oxidant sources at all the sites. [40, 41] On the other hand, we can say that NOx independent contributing sources of oxidants at all the sites can be called as more regional contributing sources of oxidants as an increase/decrease in [NOx] values does not cause an effect on oxidant concentration at all sites. The local sources depict the prevalent photochemistry at the urban site. As reported by earlier studies at urban sites the major contributor to NOx is NO₂, and in turn, the major contributor of NO₂ is the process of combustion of fuels (diesel trucks, cars, motor-generator). Nagpure et al.[45] and Badrinath et al.[46] have first reported that NO₂ concentrations in Delhi are unusually high due to increased traffic emissions by diesel trucks, even at night and also due to crop residue burning in adjoining areas of New Delhi during post monsoon and winter season (October to January). NO being a highly unstable compound gets converted to NO₂ as soon as it is produced in the troposphere.[47–48] VOC's and CO initiated chain reactions with hydroxyl and peroxy radicals present in an urban atmosphere are also the major contributors of oxidant and ozone formation at an urban site like New Delhi. These chain reactions in the troposphere catalyzes the conversion of NO and NO₂ (Eqs. (6) and (7)) and act as major contributors to the accumulation of oxidants at the site.

(R: Organic functional group).

Due to a lack in the consistency of VOC's data we were not able to further investigate the above relationship. However, we aim to further analyze this relationship in our next study.

3.5 Diurnal and monthly variation of Oxidants [OX]

The above sections of this study have established the fact that the production and accumulation of oxidants at the site are generally governed by photochemical processes. To investigate further into this relationship we have plotted averaged diurnal and monthly variation of the oxidants at all the locations of this study during the period of 2013–2019 (Fig. 10 and Fig. 11). Large variability was seen in the diurnal curve during the study period at all the sites of the study with concentrations of oxidants [OX] increasing after 0800h in the morning as the sun rises and attaining its maximum peak at noon (1200h to 1400h), and decreasing thereafter as the sun sets (after 1700hrs) (Fig. 11). This is because during noon rate of photochemical production is high as the intensity of sunlight is maximum during the noon hours in Delhi (1200h to 1400hr). Figure 12 shows the average monthly variation of oxidants at all the sites during the whole study period. It clearly shows that the maximum concentration of [OX] is observed during summer months (71.88 ppb during the month of June at CV Raman Dheerpur station) and minimum concentration is observed during winter months (37.86 ppb during the month of January at IMD Lodi Road station) (Fig. 12). Maximum values during the summer season depict enhanced photochemical activity because of high-temperature values at all the sites due to intense solar radiation and hence an increase in the number of sunny days. Minimum values during the winter season may be due to fewer sunny days which may be attributed to cloudy skies and high humidity because of frequent rainfall that may be due to frequent western disturbances occurring during this season in New Delhi during the study period, hence resulting in washout of pollutants (Fig. 16). Tiwari et al. [41] have reported similar behavior based on an observational study (SAFAR data) at a single site in New Delhi which showed maximum ozone concentrations during the summer in Delhi due to favorable meteorological conditions such as high solar intensity, clear skies, and low relative humidity. Ghude et al. [16] also reported similar behavior based on a model study. Earlier studies and this study have established that the regional and global contribution of oxidants at a site is governed by photochemistry as well as the prevailing meteorological conditions. In lieu of the above, the relationship of oxidants with temperature, humidity, wind speed and wind direction have been studied during the year 2018 and 2019 for New Delhi (5 station average) (Fig. 13, Fig. 14 and Fig. 15). Figure 13 establishes the fact that higher temperature and lower humidity values increase [OX] concentrations. Pollution rose for the years 2018 and 2019 was drawn to study [OX] concentrations. We have separated wind directions into four groups; (i) 0–90°, (ii) 90–180°, (iii) 180–270°, and (iv) 270–360° and the corresponding [OX] values were found to be 47.14 ppb, 47.19 ppb, 49.15 ppb and 50.05 respectively. Therefore it suggests that major contributors of [OX] are winds coming from the west direction into New Delhi. (Fig. 14 and Fig. 15) The sources of oxidants may be biomass burning, crop residue burning during early winter and winter months and some proportion is vehicular exhaust. When conditions were calm (wind speed ≤ 0.5 m/s) [OX] concentrations were found to be 57.84 ppb (averaged). Stagnant wind conditions do not allow the mixing of trace gases by decreasing the boundary layer height and pollutants are trapped near the surface causing a surge in the rise of ground level oxidants at all the different urban sites used in the present study.

3.6 Ozone Generation at the urban site-New Delhi-Relationship with NO_x and Temperature (5 station average)

Although the average maximum mean daytime concentration at New Delhi (5 site average) was found to be in the range of 20–30 ppb, but about ~ 2.5 % times hourly mean daytime surface ozone concentration exceeded 90 ppb (1 hourly average) marking severe pollution events in New Delhi (5 station average) under favorable conditions.

It is observed from Fig. 18 that ground-level concentration of ozone decreases with increasing NO_x concentration which is typical behavior for VOC sensitive urban conditions.[49] In the NO_x-saturated or VOC-sensitive regime, O₃ decreases with increasing NO_x and increases with increasing VOC.[50, 51]

Conclusion

This study gives a detailed analysis of surface O₃ and its interaction with its precursors like CO, NO, NO₂, and NO_x from the period of 2013 to 2019 at five different locations in New Delhi, India. This study also gives a detailed picture of the chemical interaction and coupling of O₃, NO, NO₂ and NO_x. Some salient features observed in the above study are highlighted below:

1. During the study period, the hourly averaged concentrations of O₃, NO, NO₂, CO, NO_x (NO + NO₂) and OX(NO₂ + O₃) at all the sites have been found in the range from 32.44 ppb to 36.57 ppb, 19.46 to 28.09 ppb, 20.83 to 26.89 ppb, 1.67 to 1.89 ppm, 43.04 to 54.99 ppb and 54.06 to 60.99 ppb respectively. The concentrations of NO_x and CO showed the highest values in the winter season and the lowest value in the monsoon season. The concentrations of O₃ showed the highest values in the summer season and the lowest value in the winter season.
2. The average rates of change of ozone (d[O₃]/dt) during morning hours (0800h-1100h) and in the evening hours (1700h-1900h) at Delhi (5 station average in our study) was estimated at 4.16 ppbh⁻¹ and -4.48 ppbh⁻¹, respectively. This can be because, in morning time surface O₃ formation is strongly dependent on the available amount of precursors emitted from morning vehicular traffic (0700h-1100h) and sudden change in boundary layer height with the sunrise, while the evening time loss rate (1700h-2200h) largely depends on nitrous oxide (NO) (conversion of NO₂ to NO in the evening) (Reaction 1) concentration which participates in O₃ titration processes.
3. Polynomial fit curves for NO, NO₂, and O₃ were drawn to describe the interaction and chemical coupling of the three species. (Fig 7) [NO] concentrations dominate as compared to [NO₂] and [O₃] concentrations at higher values of [NO_x] whereas at lower values of [NO_x], [O₃] dominates over [NO] and [NO₂] for all the sites used in the study as can be seen in Fig. 7. A polynomial relationship was drawn and calculated between hourly averaged NO, NO₂ and NO_x concentrations. (Fig 7) This relationship can be used in air pollution control strategies. According to Fig. 8, concentrations of hourly surface O₃ during daylight hours increases rapidly at small values of [NO₂]/[NO], this may be implicated that when O₃ was at low levels, the reactions of production of O₃ was a dominant reaction
4. The concentrations of [OX] increase with the increasing concentration of [NO_x] at all the sites of this study. Fig. 10 shows that the NO_x-dependent contribution can be equated to the local ozone

production, whereas the NO_x-independent contribution corresponds to regional or background ozone concentration. The local sources depict the prevalent photochemistry at the urban site.

5. The relationship of oxidants with temperature, humidity, and wind speed, and wind direction were studied during the years 2018 and 2019 for New Delhi. (5 station average). (Fig.13, Fig.14, Fig.15) It establishes the fact that higher temperature and lower humidity values increase concentrations of [OX]. (Fig.13) Major contributors of [OX] are winds coming from the west direction into New Delhi. (Fig. 14 and 15) The sources may be biomass burning, crop residue burning and some proportion is vehicular exhaust. When conditions were calm (wind speed ≤ 0.5 m/s) average [OX] concentrations were found to be 57.84 ppb.

Declarations

- **Availability of data and materials**

All data generated or analyzed during this study are available with India Meteorological Department, New Delhi.

- **Competing interests**

The authors declare they have no competing interests.

- **Funding**

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- **Authors' contribution**

All authors have contributed in data generation, data analysis and manuscript preparation. All authors read and approved the final manuscript.

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References

1. Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge: University Press; 2007.
2. Lefohn AS, Malley CS, Smith L, Wells B, Hazucha M, Simon H. Tropospheric ozone assessment report: Global ozone metrics for climate change, human health, and crop/ecosystem research.

- Elementa Sci Anthropocene 2018; 6:28.
3. Chameides W, Walker JCG. A photochemical theory of tropospheric ozone. *J Geophys Res* 1973; 36:8751–60.
 4. Zhang L, Jacob DJ, Boersma KF, Jaffe DA, Olson JR, Bowman KW, Worden JR, Thompson AM, Avery MA, Cohen RC, Dibb JE, Flock FM, Fuelberg HE, Huey LG, McMillan WW, Singh HB, Weinheimer AJ. Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: an integrated analysis using satellite, aircraft, ozone-sonde, and surface observations. *Atmos Chem Phys* 2008; 20:6117–36.
 5. Yadav R, Sahu LK, Jaaffrey SNA, Beig G. Distributions of ozone and related trace gases at an urban site in western India. *J Atmos Chem* 2014; 71:125–44.
 6. Sillman S, Samson PJ. Impact of temperature on oxidant photochemistry in urban, polluted rural and remote environment. *J Geophys Res* 1995; 11: 497–508.
 7. Sun Y, Wang L, Wang Y, Quan L, Zirui L. In situ measurements of SO₂, NO_x, NO_y, and O₃ in Beijing, China during august 2008. *Sci Total Environ* 2011; 409:933–40.
 8. Mavroidis I, Ilia M. Trends of NO_x, NO₂ and O₃ concentrations at three different types of air quality monitoring stations in Athens, Greece. *Atmos Environ* 2012;63: 135–47.
 9. Wayne RP. Chemistry of atmospheres: an introduction to the chemistry of the atmospheres of earth, the planets, and their satellites. Oxford: University Press New York; 2000.
 10. Census of India;2011.
 11. Economic Survey of Delhi;2018–2019.
 12. Lal S, Naja M, Subbaraya BH. Seasonal variations in surface ozone and its precursors over an urban site in India. *Atmos Environ* 2000; 17:2713–24.
 13. Saraf N, Beig G. Long term trends in tropospheric ozone over tropical regions like India. *Geophys Res Lett* 2004; 31.
 14. Badrinath KVS, Kharol SK, Kiran Chand TR, Ganga Parvathi Y, Anusuya T, Nimala Jyothsana A. Variations in black carbon aerosol, carbon monoxide and ozone over an urban area of Hyderabad, India, during the forest fire season. *Atmos Res* 2007; 85,18–26.
 15. Singla V, Satsangi A, Pachauri T, Lakhani A, Maharak Kumari K. Ozone formation and destruction at a suburban site North central region of India. *Atmos Res* 2011;101; 373–85.
 16. Ghude SD, Jain SL, Arya BC, Beig G, Ahammed YN, Kumar A, Tyagi B. Ozone in ambient air at a tropical megacity, Delhi: characteristics, trends and cumulative ozone exposure indices. *J Atmos Chem* 2008; 60:237–52.
 17. Beig G, Chate DM, Ghude SD, Mahajan AS, Srinivas R, Ali K, Sahu SK, Parkhi N, Surendran D, Trimbake HR. Quantifying the effect of air quality control measures during the 2010 Commonwealth Games at Delhi,India. *Atmos Environ* 2013; 80:455–63.
 18. Ganguly N, Tzanis C. High Surface Ozone Episodes at New Delhi, India:On a Sustainable Future of the Earth's Natural Resources. Springer: Berlin Heidelberg; 2013.p.445–53.

19. Central Pollution Control Board. Air Quality Monitoring.Emission Inventory and Source Apportionment Studies for Delhi;2010
20. Finlayson-Pitts BJ, Pitts Jr JN. Chemistry of the Upper and Lower Atmosphere. Academic Press, California; 1986. p. 4–8.
21. Chelani AB. Persistence analysis of extreme CO, NO₂ and O₃ concentrations in ambient air of Delhi. Atmos Res 2012; 108:128–34.
22. Han S, Bian H, Feng Y, Liu A, Li X, Zeng F, Zhang X. Analysis of the relationship between O₃, NO and NO₂ in Tianjin, China. Aerosol Air Qual Res 2011; 11:128–39.
23. Satsangi G, Lakhani A, Kulshrestha PR, Taneja A. Seasonal and diurnal variation of surface ozone and a preliminary analysis of exceedance of its critical levels at a semi-arid site in India. J Atmos Chem 2004; 47:271–86.
24. Sahu LK, Lal S. Distribution of C₂-C₅ NMHCs and related traces gases at a tropical urban site in India. Atmos Environ 2006; 40:880–91.
25. Beig G, Ghude SD, Polade SD, Tyagi B. Threshold exceedances and cumulative ozone exposure indices at tropical suburban site. Geophys Res Lett 2008; 35.
26. Debaje SB, Kakade AD. Surface ozone variability over western Maharashtra, India. J Hazard Mater 2009; 161:686–700.
27. Reddy BSK, Kumar KR, Balakrishnaiah G, Gopal KR, Reddy RR, Ahammed YN, Narasimhulu K, Reddy LSS, Lal S. Observational studies on the variations in surface ozone concentration at Anantapur in southern India. Atmos Res 2010; 98:125–39.
28. Naja M, Lal S, Chand D. Diurnal and seasonal variabilities in surface ozone at a high altitude site Mt Abu(24.6 N, 72.7E, 1680 m asl) in India. Atmos Environ 2003; 37:4205–15.
29. Naja M, Lal S. Surface ozone and precursor gases at Gadanki (13.5°N, 79.2°E), a tropical rural site in India. J Geophys Res 2002; 107:13.
30. Gaur A, Tripathi SN, Kanawade VP, Tare V, Shukla SP. Four-year measurements of trace gases (SO₂, NO_x, CO, and O₃) at an urban location, Kanpur, in Northern India. J Atmos Chem 2014.
31. Lal S, Naja M, Subbaraya BH. Seasonal variations in surface ozone and its precursors over an urban site in India. Atmos Environ 2000; 34:2713–24.
32. Ahammed YN, Reddy RR, Gopal KR, Narasimhulu K, Basha DB, Reddy LSS, et al. Seasonal variation of the surface ozone and its precursor gases during 2001–2003, measured at Anantapur (14_620 N), a semi-arid site in India. Atmos Res 2006; 80:151–64.
33. Sharma A, Sharma SK, Rohtash, Mandal TK. Influence of ozone precursors and particulate matter on the variation of surface ozone at an urban site of Delhi, India. Sustain Environ Res 2016; 26:76–83.
34. Pandit GG, Sahu SK, Puranik VD. Distribution and source apportionment of atmospheric non-methane hydrocarbons in Mumbai, India. Atmos Pollut Res. 2011; 2:231–36.
35. Nair PR, Chand D, Lal S, Modh KS, Naja M, Parameswaran K, et al. Temporal variations in surface ozone at Thumba (8.6_ N, 77_ E) e a tropical coastal site in India. Atmos Environ 2002; 36:603–10.

36. Nishanth T, Praseed KM, Rathnakaran K, Kumar MKS, Krishna RR, Valsaraj KT. Atmospheric pollution in a semi-urban, coastal region in India following festival seasons. *Atmos Environ* 2012; 47:295–306.
37. Ojha N, Naja M, Singh KP, Sarangi T, Kumar R, Lal S, et al. Variabilities in ozone at a semi-urban site in the Indo-Gangetic Plain region: association with the meteorology and regional processes. *J Geophys Res-Atmos* 2012; 117:1–19.
38. Sharma P, Kuniyal JC, Chand K, Guleria RP, Dhyani PP, Chauhan C. Surface ozone concentration and its behaviour with aerosols in the northwestern Himalaya, India. *Atmos Environ* 2013; 71:44–53.
39. Leighton P. Photochemistry of Air Pollution. Academies press: New York; 1961.p.300.
40. Mazzeo NA, Venegas LE, Choren H. Analysis of NO, NO₂, O₃ and NO_x concentrations measured at a green area of Buenos Aires city during wintertime. *Atmos Environ* 2005; 39:3055–68.
41. Tiwari S, Dahiya A, Kumar Nandini. Investigation into relationships among NO, NO₂, NO_x, O₃ and CO at an urban background site, Delhi, India. *Atmos Res* 2015; 157:119–26.
42. Seinfeld JH, Pandis SN. Atmospheric Chemistry and Physics. From Air Pollution to Climate Changes. Wiley: New York;1998.p.1326.
43. Clapp LJ, Jenkin ME. Analysis of the relationship between ambient levels of O₃, NO₂ and NO as a function of NO_x in the UK. *Atmos Environ* 2001; 35:6391–405.
44. Han S, Bian H, Feng Y, Liu A, Li X, Zeng F, Zhang X. Analysis of the relationship between O₃, NO and NO₂ in Tianjin, China. *Aerosol Air Qual Res* 2011; 11:128–39.
45. Nagpure AS, Sharma K, Gurjar BR. Traffic induced emission trends (2000–2005) in megacity Delhi. *Urban Clim* 2013; 4:61–73.
46. Badrinath KVS, Kharol SK, Kiran Chand TR, Ganga Parvathi Y, Anusuya T, Nimala Jyothsana A. Variations in black carbon aerosol, carbon monoxide and ozone over an urban area of Hyderabad, India, during the forest fire season. *Atmos Res* 2007; 85:18–26.
47. Carslaw DC, Beevers SD. Investigating the potential importance of primary NO₂ emissions in a street canyon. *Atmos Environ* 2004;38:3585–94.
48. Jenkin ME. Analysis of sources and portioning of oxidant in the UK-Part 2: contributions of nitrogen dioxide emissions and background ozone at a curbside location in London. *Atmos Environ* 2004; 38:5131–38.
49. Berezina E, Moiseenko K, Skorokhod A, Pankratova NV, Belikov I, Belousov V, Elansky NF. Impact of VOCs and NO_x on ozone formation in Moscow. *Atmos* 2020; 11:1262.
50. Mazzuca GM, Ren X, Loughner CP, Estes M, Crawford JH, Pickering KE, Weinheimer AJ, Dickerson RR. Ozone production and its sensitivity to NO_x and VOCs: Results from the DISCOVER-AQ field experiment, Houston 2013. *Atmos Chem Phys Discuss* 2016; 16:14463–74.
51. Sillman S, D He Some theoretical results concerning O₃-NO_x-VOC chemistry and NO_x-VOC indicators, *J Geophys Res* 2002; 107.

Figures

Figure 1

Monthly Variation of Temperature and Relative Humidity in Delhi during 2013-2019.

Figure 2

Sampling locations in New Delhi, India.

Figure 3

Variation of hourly average concentrations of NO, NO2, NOx, O3, OX and CO in Delhi.

Figure 4

Variation of monthly averaged concentration of NO, NO₂, O₃ and CO in Delhi.

Figure 5

Average rate of change of Surface Ozone ($d[O_3]/dt$) and diurnal variation of O_3 during 2013-19.

Figure 6

Hourly variation of temperature and k3 for the year 2019.

Figure 7

Variation of average daylight concentrations of O3, NO2, and NO with NOx during 2013-19.

Figure 8

Variation of O₃ concentration with the [NO₂]/[NO] ratio during 2013-19.

Figure 9

Variation of average values of [NO₂]/ [NO_x] as a function of [NO_x] (averaging time: 60 min).

Figure 10

Variation of daylight averaged values of [OX] with [NOx].

Figure 11

Variation of Hourly Averaged Concentrations of [OX] during 2013-19.

Figure 12

Variation of Monthly Averaged Concentrations of [OX] at all the sites during 2013-19.

Figure 13

Monthly variation of oxidants with Temperature and Relative Humidity (RH).

Figure 14

Frequency distribution of wind direction during the year 2018.

Figure 15

Frequency distribution of wind direction during the year 2019.

Figure 16

Frequency of western disturbances in Delhi during 2013-2019.

Figure 17

Frequency distribution curve of hourly average surface ozone concentration at New Delhi.

Figure 18

Variation of Surface Ozone during daylight hours with Temperature and NOx at New Delhi.