



Relationship of Surface Ozone (O₃) with its precursors and meteorological parameters over New Delhi, India

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सार – वर्तमान अध्ययन में 2013-2019 की अवधि में राष्ट्रीय राजधानी क्षेत्र दिल्ली में पाँच अलग-अलग स्थानों पर मॉनिटर किए गए भूतल ओजोन (O₃), नाइट्रोजन के ऑक्साइड [NO_x (NO + NO₂)], और कार्बन मोनोऑक्साइड (CO) के निरंतर माप का अध्ययन किया गया है। उपयोग किए गए पाँच निगरानी स्थानों में आईएमडी लोदी रोड, आईजीआई एयरपोर्ट पालम, सीवी रमन धीरपुर, सीआरआरआई मथुरा रोड और एनसीएमआरडब्ल्यूएफ नोएडा शामिल हैं। NO, NO₂ और सतह O₃ के बीच NO_x के कार्य के रूप में संबंधों की दिन के उजाले (0500 बजे IST से 1900 बजे IST) के दौरान जांच की गई है और तीन प्रजातियों अर्थात् NO, NO₂ और O₃ के रासायनिक युग्मन का अध्ययन किया गया है। जमीनी स्तर पर ओजोन की सांद्रता दिन के समय NO_x की मात्रा बढ़ने के साथ घटती पाई गई है। सभी अध्ययन स्थलों पर ऑक्सीडेंट में योगदान देने वाले प्रदूषण स्रोतों की जांच करने के लिए [NO_x] की सांद्रता के साथ ऑक्सीडेंट्स [OX = NO₂ + O₃] के दिन के उजाले में औसत सांद्रता में बदलाव का अध्ययन किया गया है। सभी पाँच स्थानों पर सतह O₃ सांद्रता (d O₃/dt) के परिवर्तन की औसत दर की जांच की गई है। सभी अध्ययन स्थानों पर ऑक्सीडेंट [OX] की मासिक और दैनिक भिन्नता ने तापमान के साथ एक मजबूत सकारात्मक सहसंबंध दिखाया है जबकि आर्द्रता के साथ नकारात्मक सहसंबंध है।

ABSTRACT. In the present study, continuous measurements of Surface Ozone (O₃), Oxides of Nitrogen [NO_x (NO+ NO₂)] 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, CRRM Mathura Road, and NCMRWF Noida. The relationship between NO, NO₂, and surface O₃ as a function of NO_x has been examined during daylight hours (0500 hrs IST to 1900 hrs IST) and chemical coupling of the three species, i.e., NO, NO₂ and O₃ have been studied. The ground-level concentration of Ozone has been found to decrease with increasing NO_x concentration during the daytime. The variations in daylight hourly average concentrations of oxidants [OX = NO₂ + O₃] 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 surface O₃ concentrations (dO₃/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.

Key words – Oxidants [OX], Oxides of Nitrogen, Photochemical processes, Local sources, Regional sources, Ozone Generation.

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 (O₃) changes due to the emission of O₃ precursors (e.g., oxides of nitrogen, NO_x, and carbon monoxide, CO) and has been found between + 0.25 to + 0.65 W m⁻² (with a mean value of + 0.35 W m⁻²) (Kleinman *et al.*, 2002).

Tropospheric O₃ has two main sources, namely stratosphere intrusion affecting surface O₃ (Chameides & Walker, 1973; Lefohn *et al.*, 2018) and *in situ* production via photochemical oxidation of carbon-link compounds (i.e., CO, CH₄, and VOCs), in the presence of NO_x (Chameides & Walker, 1973; Zhang *et al.*, 2008). 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, CH₄,

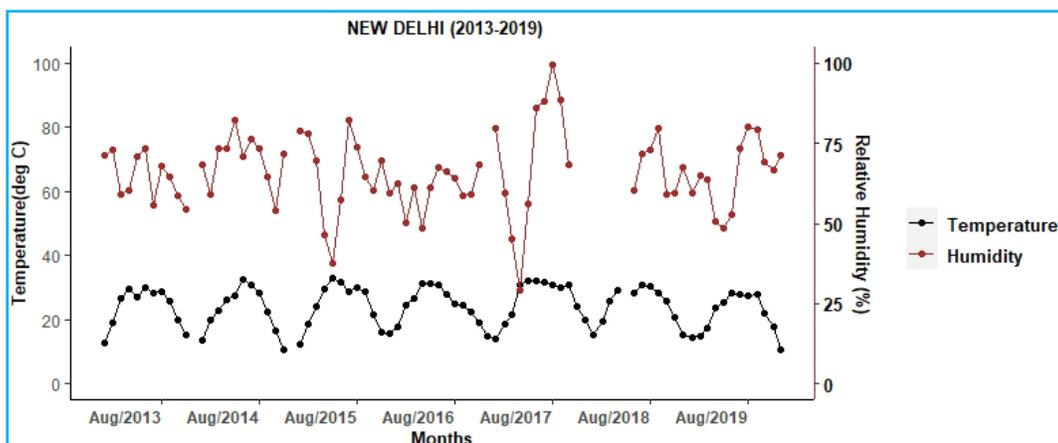


Fig. 1. Monthly variation of temperature and relative humidity in Delhi during 2013-2019

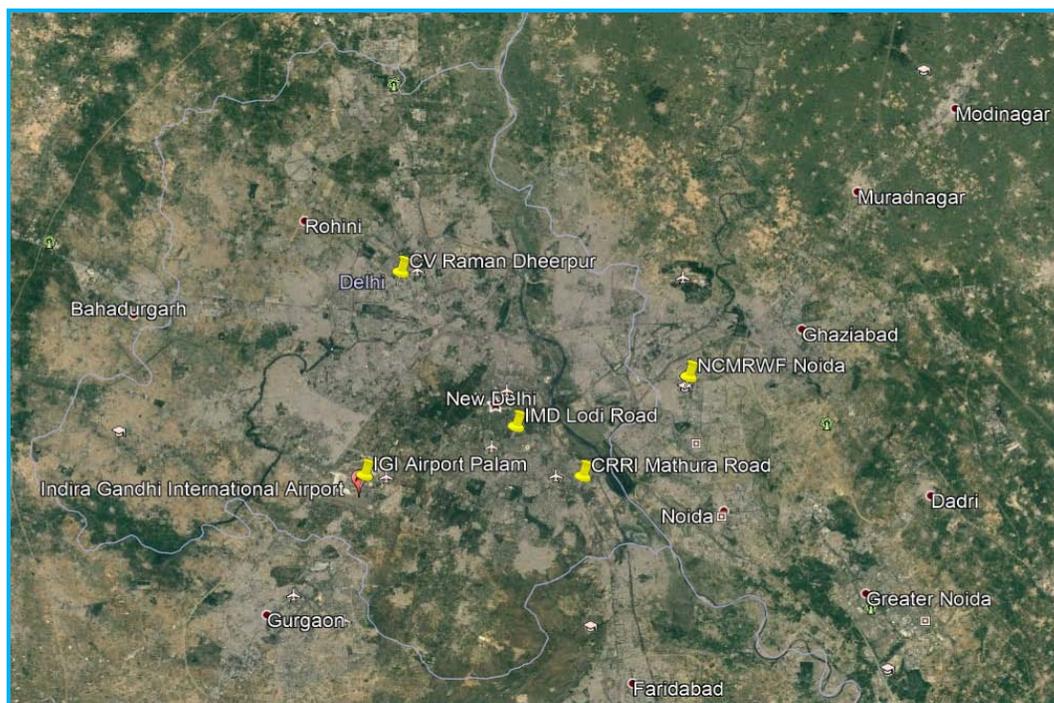


Fig. 2. Sampling locations in New Delhi, India

NMHCs, etc. in the presence of sufficient amounts of NO_x (Yadav *et al.*, 2014). 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 (Sillman & Samson, 1995). 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 (Sillman & Samson, 1995). 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) (Mavroidis & Ili, 2012; Sun *et al.*, 2011). 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. (Wayne, 1994) The oxidation begins with the reaction of Carbon monoxide

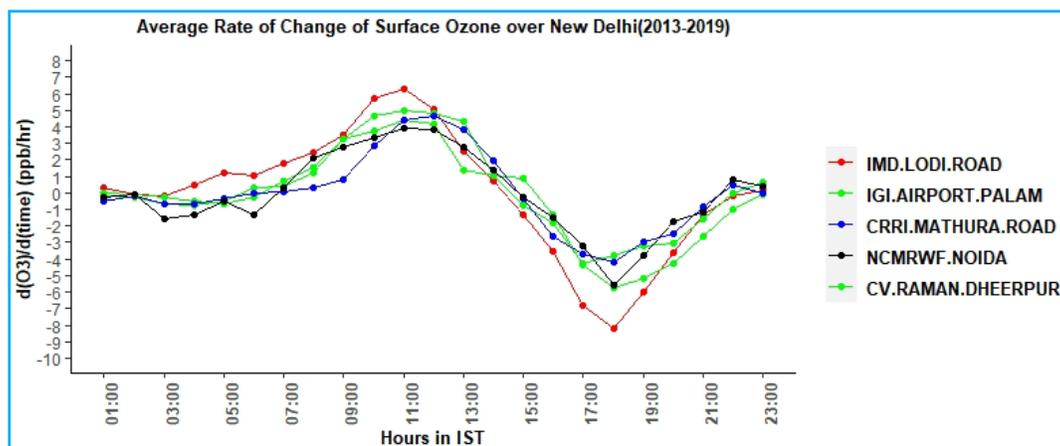


Fig. 3. Average rate of change of Surface Ozone ($d[O_3]/dt$) during 2013-19

(CO) released from various sources present in the lower troposphere with the hydroxyl radical ($\dot{O}H$), 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 $HO_2\dot{O}$. Peroxy radicals then go on to react with NO to give NO_2 which undergoes photolysis to give atomic oxygen and through reaction with oxygen (O_2) a molecule of ozone is produced in the lower troposphere.

India with a population of 1210 million (Census of India, 2011) 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%. (Census of India, 2011) As per the Census Report, (Census of India, 2011) 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. (Economic Survey of Delhi, 2008-2009) The number of vehicles per thousand in the population increased considerably from 317 in 2005-06 to 598 in 2017-18. (Economic Survey of Delhi, 2008-2009) High ozone levels have been regularly reported from major cities (Badarinath *et al.*, 2007; M. N. B. S. S Lal, 2000; Saraf & Beig, 2004; Singla *et al.*, 2011) with the capital city of New Delhi being the worst affected. (Beig *et al.*, 2013; Ganguly & Tzani, 2013; Ghude *et al.*, 2009) Surface ozone (O_3) 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 (Central Pollution Control Board, 2010). In view of the above, ambient data of NO, NO_2 , NOx, and surface O_3 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,

NO_2 and O_3 as a function of NOx ($NO + NO_2$) have been studied. In addition, the concentrations of total oxidants [OX], the sum of NO_2 and O_3 , and their relationship with NOx are also studied to understand the contributing sources of OX. The present study is an attempt to study complex coupling mechanism between NO, NO_2 and O_3 as a function of NOx and OX at five different sites for a long period of time located in the national capital of India.

2. Data, methodology and study area

Delhi is geographically located in the Northern part of India within the latitude $28^\circ 24' 17''$ to $28^\circ 53' 00''$ N, and longitude $77^\circ 45' 30''$ to $77^\circ 21' 30''$ E which is a subtropical belt. The summers in Delhi are very hot and winters are very cold. The temperature range varies from $3^\circ C$ in the winter season to $45^\circ C$ 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. Fig. 1 shows the variation of monthly average temperature and relative humidity over Delhi (5 sites average). According to the classification of seasons by the India Meteorological Department, New Delhi, 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.

TABLE 1
Observed rate of change of Surface Ozone (dO₃/dt) in different cities of India

Sites	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	(A. Sharma <i>et al.</i> , 2016)
Delhi	Urban	4.5	-5.3	(Ahammed <i>et al.</i> , 2006b)
Kanpur	Urban	3.3	-2.6	(Gaur <i>et al.</i> , 2014)
Agra	Urban	2.5	-2.4	(Singla <i>et al.</i> , 2011)
Ahmedabad	Urban	5.9	-6.4	(M. N. B. H. S. S. Lal, 2000)
Pune	Urban	4.8	-2.6	(Pandit <i>et al.</i> , 2011)
Anantapur	Rural	4.6	-2.5	(Reddy <i>et al.</i> , 2010)
Gadanki	Rural	4.6	-2.6	(Naja & Lal, 2002b)
Thumba	Coastal (Rural)	5.5	-1.4	(Nair <i>et al.</i> , 2002)
Kannur	Coastal (Rural)	4.9	-6.4	(Nishanth <i>et al.</i> , 2012)
Dayalbagh	Rural	2.2	-2.3	(Singla <i>et al.</i> , 2011)
Pantnagar	Hilly	5.6	-8.5	(Ojha <i>et al.</i> , 2012)
Mohal	Hilly	7.3	-5.9	(P. Sharma <i>et al.</i> , 2013)

* 5 stations average

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, continuously monitored air quality and meteorological data at five locations spread in different directions in Delhi have been used as these stations 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).

3. Results and discussion

3.1. Variation in rate of change of Surface O₃ at different Urban sites

Fig. 3 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 (Naja & Lal, 2002a). Urban

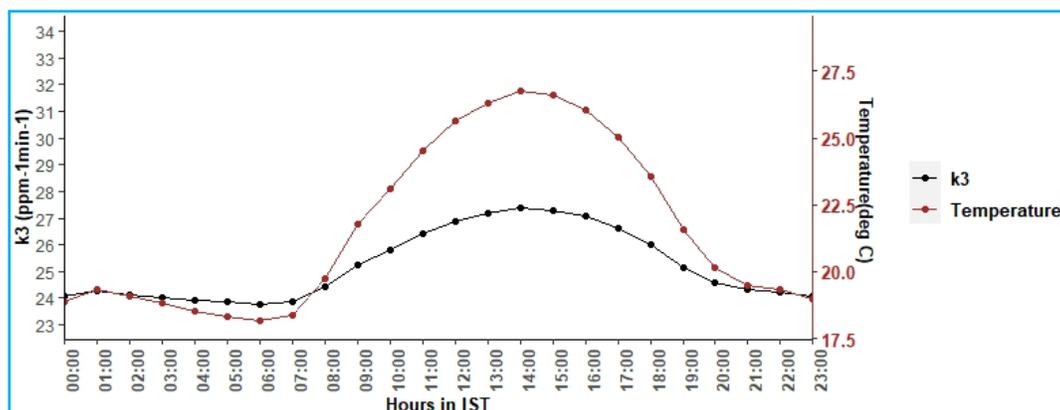
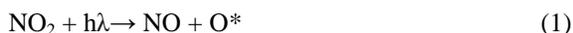


Fig. 4. Hourly variation of temperature and k_3 for the year 2019 at IMD Lodi Road

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 (Naja & Lal, 2002a). 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. The average rates of change of ozone ($d[O_3]/dt$) during morning hours (0800h-1100h) and in the evening and late evening hours (1700-1900h) at New Delhi (5 station average in our study) have been estimated at 4.16 ppbh⁻¹ and -4.48 ppbh⁻¹, respectively (Table 1). 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. (Ahammed *et al.*, 2006a; Gaur *et al.*, 2014; Lal *et al.*, 2000; Pandit *et al.*, 2011; A. Sharma *et al.*, 2016; Singla *et al.*, 2011) 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.

3.2. Chemical coupling of O₃ and its precursors

Leighton, 1961 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 Eqns. (1) and (2) are exactly opposite and canceled by the effect of Eqn. 3. It represents a null cycle where there is no net production of O₃. (Mazzeo *et al.*, 2005; Tiwari *et al.*, 2015) Therefore, these reactions as described in (Leighton, 1961) represents a closed energy system in which oxides of nitrogen (NO_x) is partitioned between its constituents, NO and NO₂ (primary NO₂), and oxidant (OX) is partitioned between its constituents NO₂ and O₃. This state is also defined as a photo stationary state (PSS). During daylight hours (as these reactions are driven by sunlight) NO, NO₂ and O₃ are at an equilibrium state for a few minutes. (Mazzeo *et al.*, 2005; Tiwari *et al.*, 2015) Hence the concentrations of the above species during PSS can be defined by the following equation (Leighton, 1961).

$$(NO)(O_3) / (NO_2) = j_1 / k_3 \quad (4)$$

j_1 is the NO₂ photolysis rate and k_3 is the rate coefficient for the reaction between NO and O₃, according to Eqn. (3) j_1 depends on the intensity of solar radiation. Rate coefficient k_3 for Eqn. (3) is temperature-dependent. It can be computed using the following equation (J. Seinfeld & Pandis, 1998).

$$k_3 (\text{ppm}^{-1} \text{min}^{-1}) = 3.23 \times 10^3 \exp(-1430/T) \quad (5)$$

Fig. 4 shows the diurnally averaged values of rate constant k_3 (ppm⁻¹min⁻¹) with average diurnal ambient air temperature of IMD Lodi Road station for the year 2019.

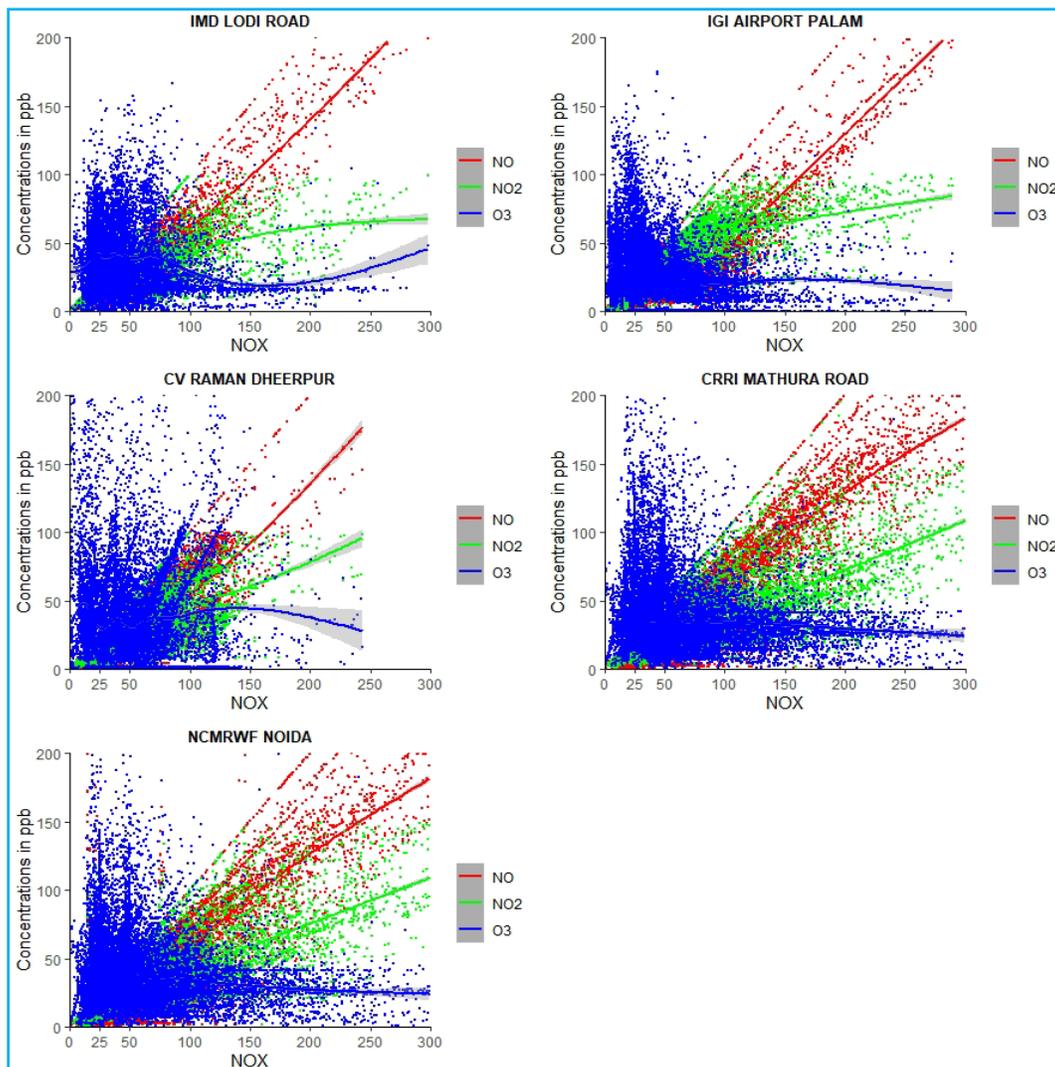


Fig. 5. Variation of average daylight concentrations of O₃, NO₂, and NO with NO_x during 2013-19

As discussed earlier, k_3 is directly proportional to temperature; therefore the maximum value of k_3 coincides with the value of maximum 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.*, $26.74 \text{ }^{\circ}\text{C}$. 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, NO₂, and O₃. The value for IMD Lodi Road station was calculated in the range of 0.58 min^{-1} to 1.87 min^{-1} with an average value of 1.02 min^{-1} .

Fig. 5 describes the relationship between O₃, NO, NO₂ with NO_x as described in the Eqns. (2) and (3) and shows the variations in the daylight (the period of sunlight)

concentrations of NO, NO₂ and O₃ 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 (Mazzeo *et al.*, 2005; Tiwari *et al.*, 2015). Polynomial fit curves for NO, NO₂ and O₃ were drawn that adequately described the interaction between the three species. As seen in Fig. 5, it can be observed that surface O₃ concentrations decrease with increasing NO_x concentrations while NO and NO₂ concentrations increase with increasing NO_x concentrations for all the stations used in this study. [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 as can be seen in Fig. 5. [O₃] and [NO] curves

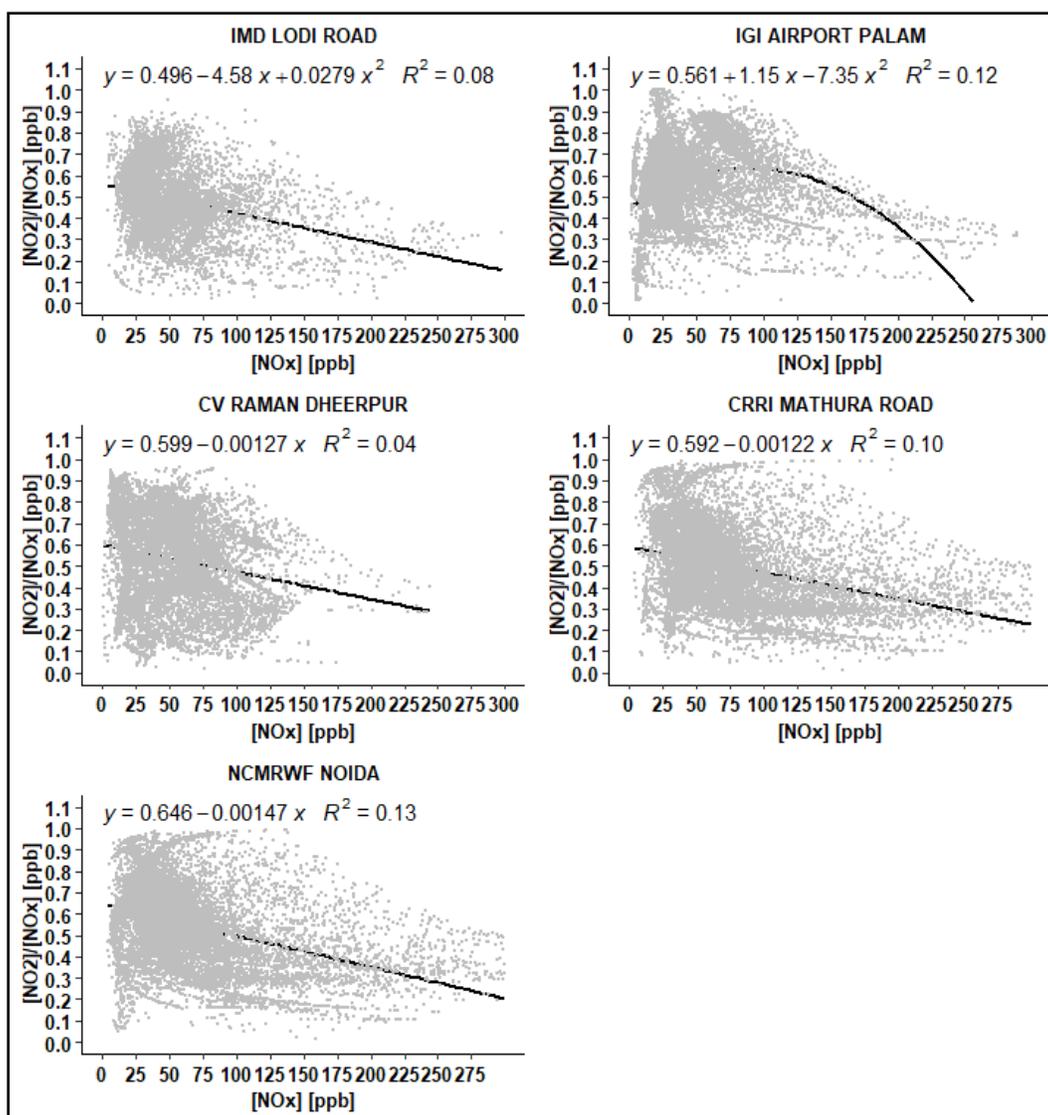


Fig. 6. Variation of average values of $[NO_2]/[NOx]$ as a function of $[NOx]$ (averaging time: 60 min)

cross over with $[NOx]$ 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. When $[NOx]$ increases $[O_3]$ values diminish but values of $[NO]$ increase as can be seen in Fig. 5 for all the sites. $[NO_2]$ and $[O_3]$ curves intersect with $[NOx]$ at values ranging between 83.067 to 85.97 ppb, maximum being for CRRM Mathura Road station as can be observed in Fig. 5. When $[NOx]$ is < 85.97 ppb $[O_3]$ is in dominant form.

Fig. 5 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 NOx , O_3 is destroyed and

NO_2 remains the predominant form of the oxidant $[OX]$. Similar behavior has been reported earlier by (Clapp & Jenkin, 2001) and (Mazzeo *et al.*, 2005) for urban and rural sites in the UK and Buenos Aires, respectively. Similar behavior has also been reported by (Tiwari *et al.*, 2015) for a single urban site in New Delhi, India.

3.3. Relationship between $[NO_2]$ and $[NOx]$

Fig. 6 presents the variation of the $[NO_2]/[NOx]$ ratio at all the locations for the whole study period (averaging time: 60 min) in the function of $[NOx]$.

It has been observed that the $[NO_2]/[NOx]$ ratio decreases with the increase of the $[NOx]$ levels.

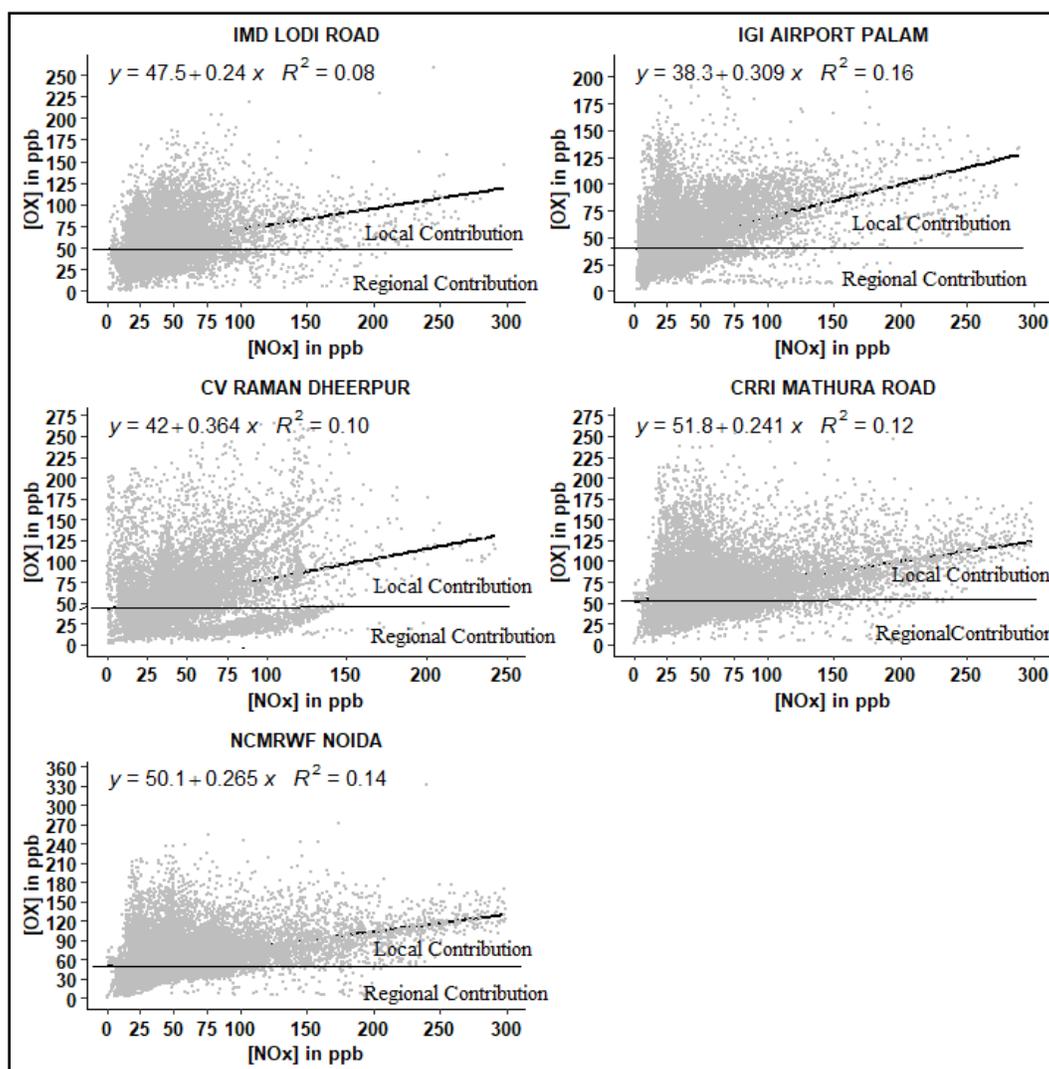


Fig. 7. Variation of daylight averaged values of [OX] with [NOx]

According to the data available, it has been calculated that for New Delhi (5 station average) when [NOx] = 100 ppb, [NO₂] / [NOx] ratio was found to be ≈ 0.296. It has been observed that mean [NO₂] concentrations for all the locations used in the study were not very high (≈ 23.24 ppb). In these cases, the average [NO₂] / [NOx] ratio for New Delhi (5 station average) was calculated to be ≈ 0.51, which is significantly higher than the ratio generally found in vehicular NOx emissions. The highest observed values of [NO₂] / [NOx] ratio at all the locations of our study for the whole study period can be explained by an additional oxidation process for NO to NO₂, possibly that of the reaction of NO with oxygen to form NO₂: [Eqn. (6)] (Clapp & Jenkin, 2001; Mazzeo *et al.*, 2005; J. H. Seinfeld & Pandis, 2006; Tiwari *et al.*, 2015).



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

Fig. 7 depicts the relationship between daylight averaged (60 min average) concentrations of oxidants [OX], *i.e.*, (NO₂ + O₃) with respect to [NOx] at all sites during the whole study period. As seen from Fig. 7 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 in 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. (Clapp & Jenkin, 2001; Mazzeo *et al.*, 2005; Tiwari *et al.*, 2015)

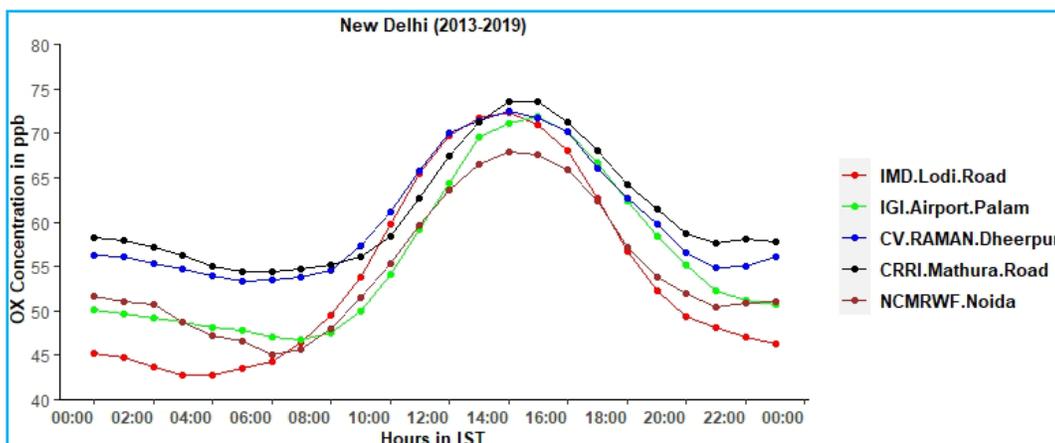


Fig. 8. Variation of Hourly Averaged Concentrations of [OX] during 2013-19

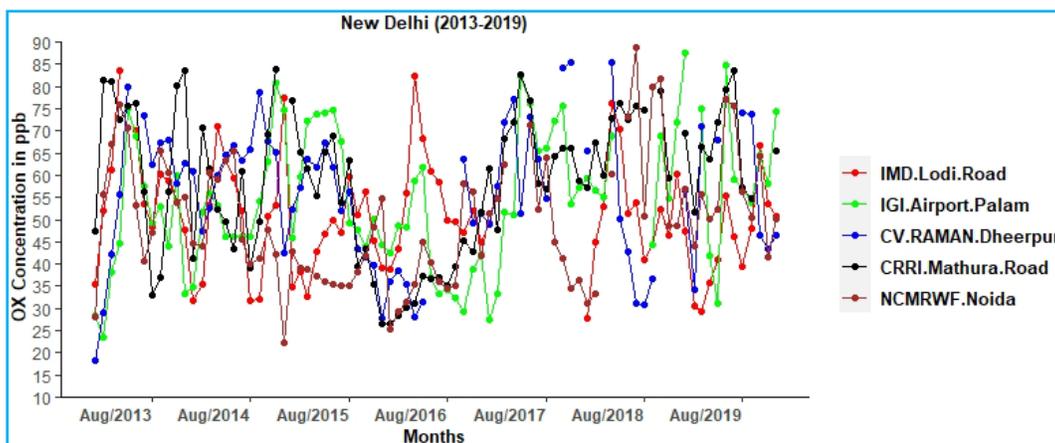


Fig. 9. Variation of Monthly Averaged Concentrations of [OX] at all the sites during 2013-19

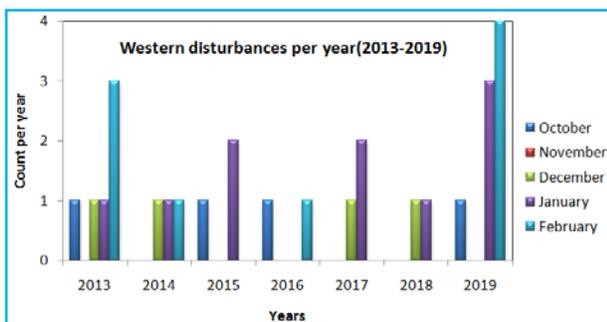


Fig. 10. Frequency of western disturbances in Delhi during 2013-2019

The NO_x-dependent contribution can be contributed to local contribution sources of oxidants and can also be correlated to primary pollutant sources. (Clapp & Jenkin, 2001; Mazzeo *et al.*, 2005; Tiwari *et al.*, 2015). It is called as [NO_x] dependant contribution because an increase/decrease in [NO_x] affects the concentration of oxidant [OX] sources at all the sites. (Mazzeo *et al.*, 2005;

Tiwari *et al.*, 2015) On the other hand, we can say that NO_x independent contributing sources of oxidants [OX] at all the sites can be called regional contributing sources of oxidants as an increase/decrease in [NO_x] values does not cause an effect on oxidant concentration [OX] 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 NO_x is NO₂ and in turn, the major contributor of NO₂ is the process of combustion of fuels (diesel trucks, cars, and motor-generator). (Nagpure *et al.*, 2013) and (Badarinath *et al.*, 2007) 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. (Carslaw & Beevers, 2004; Jenkin, 2004)

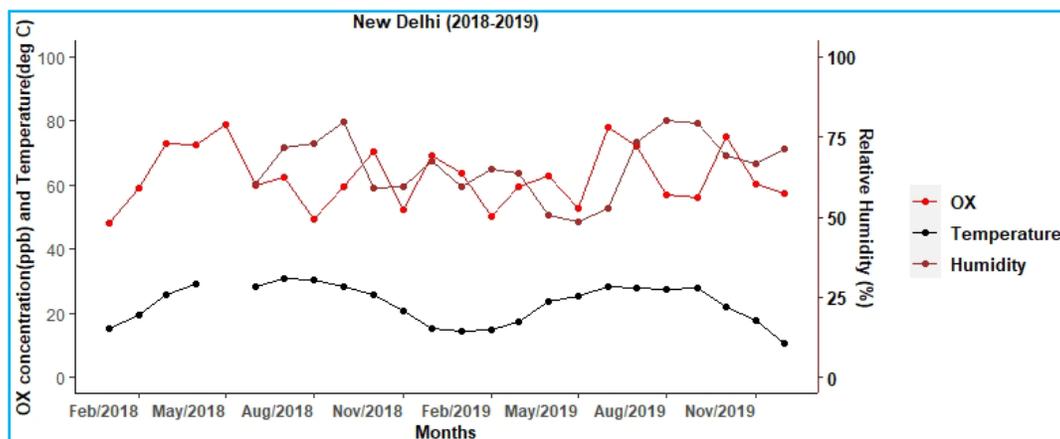
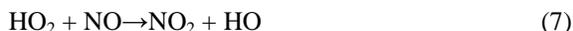


Fig. 11. Monthly averaged variation of oxidants with Temperature and Relative Humidity (RH)

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 [Eqns. (7) and (8)] 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. 8 and Fig. 9). 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. 8). This is because during noon rate of photochemical production is high as the intensity of sunlight is the maximum during noon hours in Delhi (1200h to 1400hr). Fig. 9 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 the summer months (71.88 ppb during June at CV Raman Dheerpur station) and minimum concentration is observed during winter months (37.86 ppb during January at IMD Lodi Road station) (Fig. 9). 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. 10) The relationship of oxidants with temperature and humidity has been studied during the year 2018 and 2019 for New Delhi (5 station average) (Fig. 11). Fig. 11 establishes the fact that higher temperature and lower humidity values increase [OX] concentrations. Pollution rose for the years 2018 and 2019 was also analyzed 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. 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) average [OX] concentrations were found to be 57.84 ppb. 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.

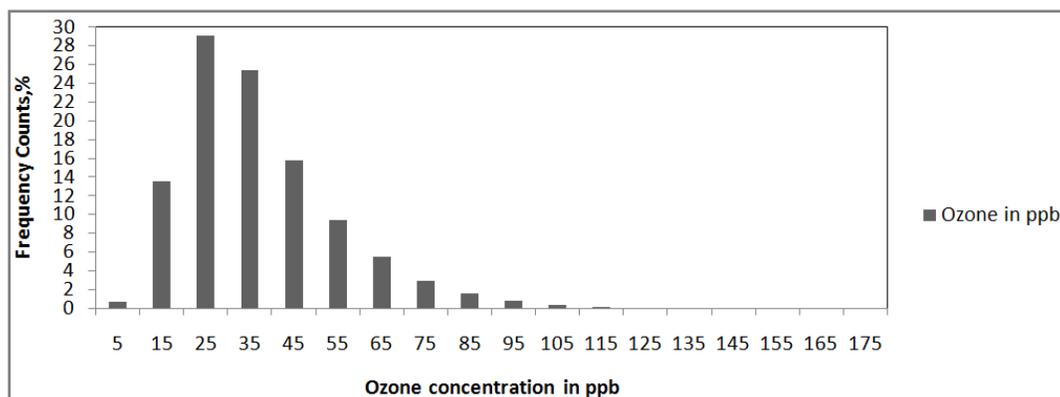


Fig. 12. Frequency distribution curve of hourly average surface ozone concentration at New Delhi

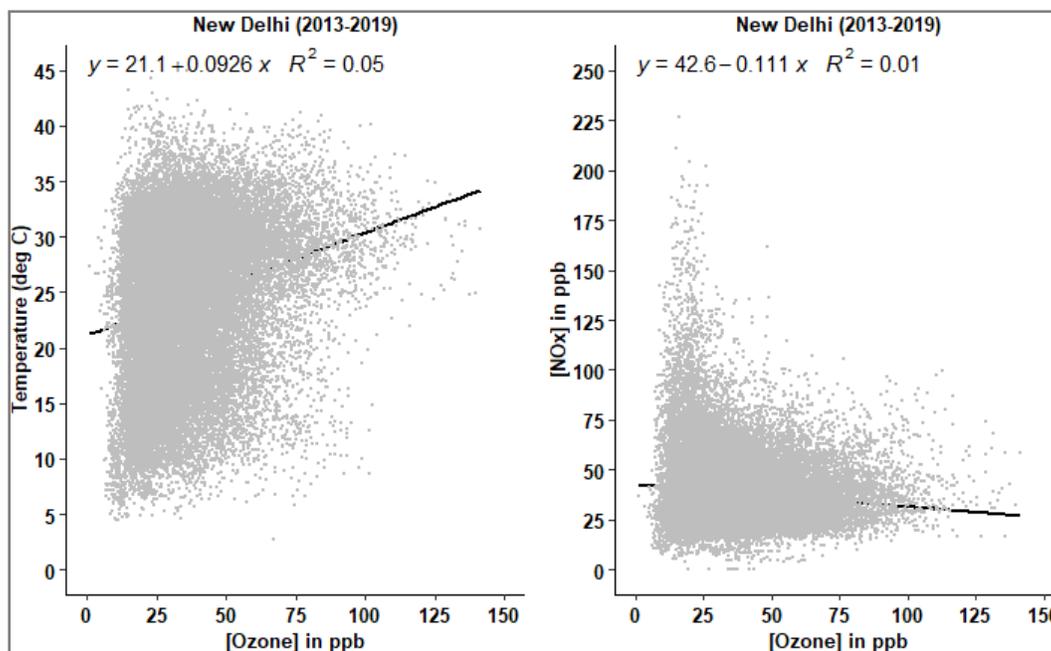


Fig. 13. Variation of hourly averaged concentrations of surface ozone with NO_x and temperature

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 (Fig. 12).

It is observed from Fig. 13 that ground-level concentration of ozone (averaging time :60 min) decreases

with increasing NO_x concentration which is typical behaviour for VOC sensitive urban conditions (Berezina *et al.*, 2020). In the NO_x-saturated or VOC-sensitive regime, O₃ decreases with increasing NO_x and increases with increasing VOC. (Mazzuca *et al.*, 2016; Sillman & He, 2002).

4. 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:

(i) 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) concentration which participates in O₃ titration processes.

(ii) Polynomial fit curves for NO, NO₂ and O₃ were drawn to describe the interaction and chemical coupling of the three species. (Fig. 5) [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. 5. The polynomial curve explained the chemical coupling and interaction between the three species as explained by the equation of PSS. [Eqn. (3)].

(iii) Fig. 7 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.

(iv) The relationship of oxidants with temperature, humidity, wind speed and wind direction were studied during the years 2018 and 2019 for New Delhi. (5 station average) and it established the fact that higher temperature and lower humidity values increase concentrations of [OX]. Major contributors of [OX] are winds coming from the west direction into New Delhi. When conditions were calm (wind speed ≤ 0.5 m/s) average [OX] concentrations were found to be 57.84 ppb.

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References

- Ahamed, Y. N., Reddy, R. R., Gopal, K. R., Narasimhulu, K., Basha, D. B., Reddy, L. S. S. and Rao, T. V. R., 2006a, "Seasonal variation of the surface ozone and its precursor gases during 2001-2003, measured at Anantapur (14.62°N), a semi-arid site in India", *Atmospheric Research*, **80**, 2-3, 151-164.
- Ahamed, Y. N., Reddy, R. R., Gopal, K. R., Narasimhulu, K., Basha, D. B., Reddy, L. S. S. and Rao, T. V. R., 2006b, "Seasonal variation of the surface ozone and its precursor gases during 2001-2003, measured at Anantapur (14.62°N), a semi-arid site in India", *Atmospheric Research*, **80**, 2-3, 151-164. <https://doi.org/10.1016/J.ATMOSRES.2005.07.002>.
- Badarinath, K. V. S., Kumar Kharol, S., Kiran Chand, T. R., Parvathi, Y. G., Anasuya, T. and Jyothsna, A. N., 2007, "Variations in black carbon aerosol, carbon monoxide and ozone over an urban area of Hyderabad, India, during the forest fire season", *Atmospheric Research*, **85**, 1, 18-26. <https://doi.org/10.1016/J.ATMOSRES.2006.10.004>.
- Beig, G., Chate, D. M., Ghude, S. D., Mahajan, A. S., Srinivas, R., Ali, K., Sahu, S. K., Parkhi, N., Surendran, D. and Trimbake, H. R., 2013, "Quantifying the effect of air quality control measures during the 2010 Commonwealth Games at Delhi, India", *Atmospheric Environment*, **80**, 455-463. <https://doi.org/10.1016/J.ATMOSENV.2013.08.012>.
- Berezina, E., Moiseenko, K., Skorokhod, A., Pankratova, N. V., Belikov, I., Belousov, V. and Elansky, N. F., 2020, "Impact of VOCs and NO_x on Ozone Formation in Moscow", *Atmosphere* **2020**, **11**, p1262. <https://doi.org/10.3390/ATMOS11111262>.
- Carslaw, D. C. and Beevers, S. D., 2004, "Investigating the potential importance of primary NO₂ emissions in a street canyon", *Atmospheric Environment*, **38**, 22, 3585-3594.
- Census of India: Provisional Population Totals India : Paper1 : Census 2011, (n.d.). Retrieved August 26, 2021, from https://censusindia.gov.in/2011-prov-results/prov_results_paper1_india.html.
- Chameides, W. and Walker, J. C. G., 1973, "A photochemical theory of tropospheric ozone", *Journal of Geophysical Research*, **78**, 36, 8751-8760. <https://doi.org/10.1029/JC078I036P08751>.
- Clapp, L. J. and Jenkin, M. E., 2001, "Analysis of the relationship between ambient levels of O₃, NO₂ and NO as a function of NO_x in the UK", *Atmospheric Environment*, **35**, 36, 6391-6405.
- CPCB, Central Pollution Control Board. (n.d.). Retrieved August 26, 2021, from <https://cpcb.nic.in/source-apportionment-studies/>.
- Economic Survey of Delhi 2008-2009, Planning Department, (n.d.). Retrieved August 26, 2021, from <http://delhiplanning.nic.in/content/economic-survey-delhi-2008-2009>.
- Ganguly, N. D. and Tzani, C., 2013, "High Surface Ozone Episodes at New Delhi, India", On a Sustainable Future of the Earth's, *Natural Resources*, 445-453. https://doi.org/10.1007/978-3-642-32917-3_26.
- Gaur, A., Tripathi, S. N., Kanawade, V. P., Tare, V. and Shukla, S. P., 2014, "Four-year measurements of trace gases (SO₂, NO_x, CO, and O₃) at an urban location, Kanpur, in Northern India", *Journal of Atmospheric Chemistry*, **71**, 4, 283-301. <https://doi.org/10.1007/S10874-014-9295-8/EMAIL/CORRESPONDENT/C2/NEW>.
- Ghude, S. D., Jain, S. L., Arya, B. C., Beig, G., Ahamed, Y. N., Kumar, A. and Tyagi, B., 2009, "Ozone in ambient air at a tropical megacity, Delhi : characteristics, trends and cumulative

- ozone exposure indices”, *Journal of Atmospheric Chemistry*, **60**, 3, 237-252. <https://doi.org/10.1007/S10874-009-9119-4>.
- Jenkin, M. E., 2004, “Analysis of sources and partitioning of oxidant in the UK-Part 2 : contributions of nitrogen dioxide emissions and background ozone at a kerbside location in London”, *Atmospheric Environment*, **38**, 30, 5131-5138. <https://doi.org/10.1016/J.ATMOSENV.2004.05.055>.
- Kleinman, L. I., Daum, P. H., Lee, Y. N., Nunnermácker, L. J., Springston, S. R., Weinstein-Lloyd, J. and Rudolph, J., 2002, “Ozone production efficiency in an urban area”, *Journal of Geophysical Research Atmospheres*, **107**, 23, <https://doi.org/10.1029/2002JD002529>.
- Lal, S., Naja, M. and Subbaraya, B. H., 2000, “Seasonal variations in surface ozone and its precursors over an urban site in India”, *Atmospheric Environment*, **34**, 17, 2713-2724. [https://doi.org/10.1016/S1352-2310\(99\)00510-5](https://doi.org/10.1016/S1352-2310(99)00510-5).
- Lefohn, A. S., Malley, C. S., Smith, L., Wells, B., Hazucha, M., Simon, H., Naik, V., Mills, G., Schultz, M. G., Paoletti, E., De Marco, A., Xu, X., Zhang, L., Wang, T., Neufeld, H. S., Musselman, R. C., Tarasick, D., Brauer, M., Feng, Z., Tang, H., Kobayashi, K., Sicard, P., Solberg, S. and Gerosa, G., 2018, “Tropospheric ozone assessment report : Global ozone metrics for climate change, human health, and crop/ecosystem research”, *Elementa*, **6**. <https://doi.org/10.1525/elementa.279>.
- Leighton, P., 1961, “Photochemistry of Air Pollution 1st Edition (1st ed.)”, Academic Press. <https://www.elsevier.com/books/photochemistry-of-air-pollution/leighton/978-0-12-442250-6>.
- Mavroidis, I. and Iliá, M., 2012, “Trends of NO_x, NO₂ and O₃ concentrations at three different types of air quality monitoring stations in Athens, Greece”, *Atmospheric Environment*, **63**, 135-147. <https://doi.org/10.1016/J.ATMOSENV.2012.09.030>.
- Mazzeo, N. A., Venegas, L. E. and Choren, H., 2005, “Analysis of NO, NO₂, O₃ and NO_x concentrations measured at a green area of Buenos Aires City during wintertime”, *Atmospheric Environment*, **39**, 17, 3055-3068.
- Mazzuca, G. M., Ren, X., Loughner, C. P., Estes, M., Crawford, J. H., Pickering, K. E., Weinheimer, A. J. and Dickerson, R. R., 2016, “Ozone production and its sensitivity to NO_x and VOCs: Results from the DISCOVER-AQ field experiment, Houston 2013”, *Atmospheric Chemistry and Physics*, **16**, 22, 14463-14474. <https://doi.org/10.5194/ACP-16-14463-2016>.
- Nagpure, A. S., Sharma, K. and Gurjar, B. R., 2013, “Traffic induced emission estimates and trends (2000-2005) in megacity Delhi”, *Urban Climate*, **4**, 61-73. <https://doi.org/10.1016/J.UCLIM.2013.04.005>.
- Nair, P. R., Chand, D., Lal, S., Modh, K. S., Naja, M., Parameswaran, K., Ravindran, S. and Venkataramani, S., 2002, “Temporal variations in surface ozone at Thumba (8.6 °N, 77 °E) - a tropical coastal site in India”, *Atmospheric Environment*, **36**, 4, 603-610.
- Naja, M. and Lal, S., 2002a, “Surface ozone and precursor gases at Gadanki (13.5 °N, 79.2 °E), a tropical rural site in India”, *Journal of Geophysical Research Atmospheres*, **107**, 14, ACH 8-1-ACH 8-13. <https://doi.org/10.1029/2001JD000357>.
- Naja, M. and Lal, S., 2002b, “Surface ozone and precursor gases at Gadanki (13.5 °N, 79.2 °E), a tropical rural site in India”, *Journal of Geophysical Research : Atmospheres*, **107**(D14), ACH 8-1. <https://doi.org/10.1029/2001JD000357>.
- Nishanth, T., Praseed, K. M., Rathnakaran, K., Satheesh Kumar, M. K., Ravi Krishna, R. and Valsaraj, K. T., 2012, “Atmospheric pollution in a semi-urban, coastal region in India following festival seasons”, *Atmospheric Environment*, **47**, 295-306. <https://doi.org/10.1016/J.ATMOSENV.2011.10.062>.
- Ojha, N., Naja, M., Singh, K. P., Sarangi, T., Kumar, R., Lal, S., Lawrence, M. G., Butler, T. M. and Chandola, H. C., 2012, “Variabilities in ozone at a semi-urban site in the Indo-Gangetic Plain region : Association with the meteorology and regional processes”, *Journal of Geophysical Research : Atmospheres*, **117**(D20), 20301. <https://doi.org/10.1029/2012JD017716>.
- Pandit, G. G., Sahu, S. K. and Puranik, V. D., 2011, “Distribution and source apportionment of atmospheric non-methane hydrocarbons in Mumbai, India”, *Atmospheric Pollution Research*, **2**, 2, 231-236. <https://doi.org/10.5094/APR.2011.029>.
- Reddy, B. S. K., Kumar, K. R., Balakrishnaiah, G., Gopal, K. R., Reddy, R. R., Ahammed, Y. N., Narasimhulu, K., Reddy, L. S. S. and Lal, S., 2010, “Observational studies on the variations in surface ozone concentration at Anantapur in southern India”, *Atmospheric Research*, **98**, 1, 125-139.
- Saraf, N. and Beig, G., 2004, “Long-term trends in tropospheric ozone over the Indian tropical region”, *Geophysical Research Letters*, **31**, 5. <https://doi.org/10.1029/2003GL018516>.
- Seinfeld, J. H. and Pandis, S. N., 2006, “Atmospheric chemistry and physics from air pollution to climate change”, J. Wiley, New York. <http://vlib.kmu.ac.ir/kmu/handle/kmu/82106>.
- Seinfeld, J. and Pandis, S., 1998, “Atmospheric chemistry and physics”, From Air Pollution to Climate Changes.
- Sharma, A., Sharma, S. K., Rohtash and Mandal, T. K., 2016, “Influence of ozone precursors and particulate matter on the variation of surface ozone at an urban site of Delhi, India”, *Sustainable Environment Research*, **26**, 2, 76-83. <https://doi.org/10.1016/j.serj.2015.10.001>.
- Sharma, P., Kuniyal, J. C., Chand, K., Guleria, R. P., Dhyani, P. P. and Chauhan, C., 2013, “Surface ozone concentration and its behaviour with aerosols in the northwestern Himalaya, India”, *Atmospheric Environment*, **71**, 44-53. <https://doi.org/10.1016/J.ATMOSENV.2012.12.042>.
- Sillman, S. and He, D., 2002, “Some theoretical results concerning O₃-NO_x-VOC chemistry and NO_x-VOC indicators”, *Journal of Geophysical Research : Atmospheres*, **107**(D22), ACH 26-1. <https://doi.org/10.1029/2001JD001123>.
- Sillman, S. and Samson, P. J., 1995, “Impact of temperature on oxidant photochemistry in urban, polluted rural and remote environments”, *Journal of Geophysical Research : Atmospheres*, **100**(D6), 11497-11508. <https://doi.org/10.1029/94JD02146>.
- Singla, V., Satsangi, A., Pachauri, T., Lakhani, A. and Kumari, K. M., 2011, “Ozone formation and destruction at a sub-urban site in North Central region of India”, *Atmospheric Research*, **101**, 1-2), 373-385. <https://doi.org/10.1016/J.ATMOSRES.2011.03.011>.
- Sun, Y., Wang, L., Wang, Y., Quan, L. and Zirui, L., 2011, “In situ measurements of SO₂, NO_x, NO_y, and O₃ in Beijing, China during August 2008”, *Science of The Total Environment*, **409**, 5), 933-940. <https://doi.org/10.1016/J.SCITOTENV.2010.11.007>.
- Tiwari, S., Dahiya, A. and Kumar, N., 2015, “Investigation into relationships among NO, NO₂, NO_x, O₃, and CO at an urban background site in Delhi, India”, *Atmospheric Research*, **157**, 119-126. <https://doi.org/10.1016/j.atmosres.2015.01.008>.

Wayne, R. P., 1994, "Atmospheric Chemistry : Introduction", *Low-Temperature Chemistry of the Atmosphere*, 1-20. https://doi.org/10.1007/978-3-642-79063-8_1.

Yadav, R., Sahu, L. K., Jaaffrey, S. N. A. and Beig, G., 2014, "Distributions of ozone and related trace gases at an urban site in western India", *Journal of Atmospheric Chemistry*, **71**, 2, 125-144. <https://doi.org/10.1007/S10874-014-9286-9/EMAIL/CORRESPONDENT/C1/NEW>.

Zhang, L., Jacob, D. J., Boersma, K. F., Jaffe, D. A., Olson, J. R., Bowman, K. W., Worden, J. R., Thompson, A. M., Avery, M. A., Cohen, R. C., Dibb, J. E., Flock, F. M., Fuelberg, H. E., Huey, L. G., McMillan, W. W., Singh, H. B. and Weinheimer, A. J., 2008, "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, ozonesonde, and surface observations", *Atmospheric Chemistry and Physics*, **8**, 20, 6117-6136. <https://doi.org/10.5194/acp-8-6117-2008>.

