



Assessment of Variations and Correlation of Ozone and its Precursors, Benzene, Nitrogen Dioxide, Carbon monoxide and some Meteorological Variables at two Sites of Significant Spatial Variations in Delhi, Northern India

Ram Chhavi Sharma^{1*} and Niharika Sharma²

1. Department of Physics, Faculty of Science, Shree Guru Gobind Singh Tricentenary University, Gurugram-122505, Haryana, India

2. Department of Chemistry, Govt. Senior Secondary School, Bhangrola Gurugram-122505, Haryana, India

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ABSTRACT

Ozone(O₃), and its precursors, Benzene (C₆H₆), Nitrogen Dioxide(NO₂), Carbon Monoxide (CO) and meteorological parameters Temperature, Relative Humidity and Wind Speed were measured in urban air of two sites of significant spatial variations, Delhi Milk Scheme (DMS), Sadipur and Netaji Subhash Chander Institute of Technology(NSIT) Dwarka, during 2017–2018. Samples collected by Central Pollution Control Board (CPCB) has been analysed. The concentrations of Benzene, Nitrogen dioxide and Carbon monoxide were found to be more at DMS than NSIT site in winter season (11.137±3.258, 5.540±1.441, 55.333±12.741, 44.667±10.066µg/m³, 1.433±0.058, 1.033±0.287mg/m³ respectively) and summer season (3.167±1.222, 2.233±0.929, 50.333±2.082, 31.333±6.658µg/m³, 0.743±0.151, 0.443±0.051mg/m³ respectively) while Ozone was found to be more at NSIT than DMS site (40.333±3.215, 34.433±2.503µg/m³ respectively). The maximum concentrations of Benzene for the DMS and NSIT sites, respectively, were 32.4µg/m³ and 17.7µg/m³ and was observed in the month of November while minimum were 1.0µg/m³ and 0.6µg/m³ and was observed in the month of June. For Ozone, the maximum concentrations for the DMS and NSIT sites, respectively, were 100µg/m³ and 101µg/m³ and was observed in the month of June while minimum were 33.0µg/m³ and 28.0µg/m³ and was observed in the month of February and December respectively. Regression analyses were performed to correlate O₃ concentrations with C₆H₆, NO₂ and CO in order to infer their possible sources. The study reveals that there is significant correlation of O₃ with C₆H₆ (r²=0.475) and CO (r²=0.985) in summer at DMS and with C₆H₆ (r²=0.902) & NO₂(r²=0.728) in winter at NSIT. The correlation of O₃, C₆H₆, NO₂ and CO with Temperature, Relative Humidity and Wind Speed has also been investigated to understand their influence on these pollutants.

KEYWORDS: Air pollution; tropospheric ozone; benzene; regression; precursors.

INTRODUCTION

Surface ozone (O₃) is an important trace gas in the lower troposphere which plays a key role in enhancing the oxidizing capacity of the atmosphere and exerts adverse effects on human health as well as damages ecosystem and agricultural crops (Wang et al., 2003, Garcia et al., 2005, Mittal et al., 2007, Jerrett et al., 2009, Niishanth et al., 2014, Faridi et al., 2018). It is a secondary air pollutant because its formation occurs in the presence of sunlight and its precursors, i.e.,

* Corresponding Author, Email: ramchhavisharma@yahoo.com, rcsharma@sgtuniversity.org

Benzene (C₆H₆), Nitrogen Oxides (NO_x), Carbon monoxide (CO) etc., which control the budget of tropospheric O₃ (Garcia et al., 2005). The mixing ratio of O₃ may be directly affected by the changes in photolysis rate constant and indirectly by the NO_x and HO_x budget modifications. As a consequence, the NO destroys O₃, forming NO₂ through photolysis.

Benzene has been recognized as toxic air pollutants (Chou et al., 2011, Pires, 2012, Pusede & Cohin 2012). It exists in air predominantly in the vapour phase, with residence time varying between few hours to a few days depending on the environment and climate. Degradation of benzene in air occurs mainly by reaction with hydroxyl, alkoxy and peroxy radicals. The importance of Benzene and other Volatile Organic Compounds (VOCs) in the lower atmosphere is that they are precursors of O₃, some of them are toxic to humans, and they have multiple and different sources (Ainsworth et al., 2012). Its presence in the troposphere changes the natural cycle of formation and destruction of O₃ by reacting to form radicals, which either consume NO or convert NO to NO₂ resulting the accumulation of a part of O₃ in the atmosphere (National Research Council, 1991).

CO has been recognized as toxic air pollutants and precursor of O₃. The chemical reactions involved in tropospheric ozone formation are a series of complex cycles in which carbon monoxide and VOCs are oxidized to water vapour and carbon dioxide. The oxidation begins with the reaction of CO with the hydroxyl radical (OH) (Reeves, Claire et al., 2002). The radical intermediate formed by this reacts rapidly with oxygen to give a peroxy radical HO₂. Peroxy-radicals then go on to react with NO to produce NO₂, which is photo dissociated by UV-A radiation to give a ground state atomic oxygen, which then reacts with molecular oxygen to form ozone (Sharma & Sharma 2017).

In urban areas, O₃ is mainly formed from complex photochemical interactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The controls of NO_x emissions will decrease ozone formation in areas with the NO_x-sensitive regime but increase ozone formation in VOC-sensitive areas (Mazzuca et al., 2016, Sharma et al., 2016, Chang et al., 2016, Karl et al., 2017, Goldberg et al., 2016).

One method of estimating ozone sensitivity to precursor emissions with the aid of chemical transport models is by examining the ratios of certain species (i.e. indicator ratios) that are different for NO_x-sensitive and VOC-sensitive conditions (Sillman et al. 1999). The study of correlation between O₃ and its precursors help to better understand the chemistry of ozone and other components of photochemical smog and also to design more effective control strategies to reduce O₃ concentrations. (Kinga Wałaszek et al., 2018).

Meteorology plays an important role in air pollutants formation, dispersion, transport and dilution. Therefore, the variations in local meteorological conditions, such as wind speed, wind direction, temperature and relative humidity (RH), can affect the temporal variation of surface O₃ and its precursors ((Nishanth et al., 2014, Sharma and Sharma, 2016, Sharma, R.C. 2020).

Thus in order to reduce O₃ concentrations, it is necessary to control the emissions of its precursors and hence their sources. Benzene is released into the environment from both natural and man-made sources, although the later is the most significant source. The main sources contributing in Delhi to Benzene emissions are regional sources and mobile sources (Sillman 1999). The content of Benzene in gasoline is usually 25% to 30% [Trail et al., 2014, Geng et al., 2008).

Many studies on C₆H₆ in urban and rural atmosphere have been carried out around the world (Keymeulen et al., 2001; Barletta et al., 2005; Parra et al., 2006; Velasko et al., 2007; Tiwari et al., 2010; Miller et al., 2011; Civan et al., 2011; Shaw et al., 2015). However, only few studies carried out in urban location in India (Garg et al., 2019, Chaudhary et al., 2012) and there is still a substantial lack of information on C₆H₆ abundance and spatial localization.

In the present study, two sites Delhi Milk Scheme(DMS), Sadipur, Patel Nagar, a mixed region and Netaji Subhash Chander Institute of Technology(NSIT), Dwarka, developed as a smart city, in Delhi, the National Capital of India has been selected. This study aims to investigate the variation in O_3 with its precursors C_6H_6 , NO_2 and CO in ambient air of two urban sites located in Delhi, during winter and summer seasons in 2017-2018. The main objectives of this research were as follows: (1) to assess seasonal variation of O_3 , C_6H_6 , NO_2 and CO in regions of different topology (2) to correlate concentrations of O_3 with concentrations of air pollutants C_6H_6 , NO_2 and CO to infer how these pollutants influences the natural cycle of formation and destruction of O_3 (3) to correlate concentrations of air pollutants O_3 , C_6H_6 , NO_2 and CO with meteorological parameters such as Temperature, Relative Humidity and Wind Speed to infer their influences on concentrations of these pollutants.

MATERIALS AND METHODS

The study has been conducted at two sites Delhi Milk Scheme(DMS) and Netaji Subhash Chander Institute of Technology(NSIT) Dwarka, of Delhi, the national capital of India (Fig. 1). DMS monitoring station is located in Sadipur, Patel Nagar subdivision of West Delhi administrative districts ($28^{\circ} 39' 07''N$, $77^{\circ} 09' 27''E$). West Delhi is bound by the districts of North West Delhi to the north, North Delhi and Central Delhi to the east, South West Delhi to the south, and Jhajjar District of Haryana state to the west. West Delhi has an area of 129 km^2 , with a population density of 19,625 inhabitants per square kilometre. Patel Nagar subdivision of West Delhi district has total population of 1,262,158 as per the Census 2011 and its population growth rate over the decade 2001-2011 was 18.91%. It is a mixed region having industrial, commercial and residential activities. Major residential and commercial areas of Delhi like Janakpuri and Tilaknagar are located in this district while industrial and commercial areas Mayapuri and Naraina are in neighbourhood.

The area is serviced by a depot for the Delhi Transport Corporation (DTC), Shadipur Station of Delhi Metro and a number of petrol pumps. Close to it lies an important intersection, where average number of vehicles on a typical summer evening passing through the intersection per green signal is 280. The number of cars and buses that populate that stretch of the signal is about 148. The signal of the previous intersection is also usually synchronized with this one.

NSIT monitoring station is located in Dwarka (Latitude $28^{\circ} 40' N$ and $28^{\circ} 29' N$ and Longitude between $76^{\circ} 50' E$ and $77^{\circ} 14' E$) which is a sub-city of South west District of Delhi, and a diplomatic enclave. Dwarka is being developed as residential green area and a smart city under Delhi Development Authority's 'smart sub-city' project. The main source of pollution in the study area are excessive construction and demolition activities, vehicular emission, domestic cooking, stubble burning in the neighboring states, industrial emission and commercial activities in the surrounding areas and other man made perturbation on account of excessive population loading (Sharma, R. C. 2020).

In order to identify the concentrations of O_3 , C_6H_6 , NO_2 and CO , an online continuous monitoring system, also known as Continuous Ambient Air Quality Monitoring System (CAAQMS) have been used (CPCB, 2003). The CPCB has laid down the national guidelines for the monitoring and chemical analysis of BTX in ambient air through CAAQMS by using Gas Chromatography (GC) (CPCB, 2012). The concentrations of C_6H_6 on online continuous monitoring system were analysed by chromatographic separation in the gaseous phase followed by their detection using a Photo Ionization Detector (PID). For the comparative analysis of summer and winter seasons, the data have been analysed from November 2017 to June 2018

which includes the winter and summer seasons. For the statistical analysis, the Microsoft Excel and MINITAB software were used to analyze the data. Descriptive statistics have been used to find out the range of concentration, mean concentration and standard deviation (Garg et al., 2019). The linear regression analysis has been used to correlate the ozone with its precursors C_6H_6 , NO_2 and CO, and also with meteorological variables temperature, relative humidity and wind speed.



Fig. 1. Spatial location of DMS and NSIT Continuous Air Quality Monitoring Stations, operated by Central Pollution Control Board (CPCB), Delhi.

RESULTS AND DISCUSSION

In this study, we have analysed and correlated the O_3 and its precursors C_6H_6 , NO_2 and CO concentrations obtained at two sites in mega city Delhi, in Northern India for winter and summer seasons for the period from November 2017 to June 2018. The O_3 , C_6H_6 , NO_2 and CO seasonal variations and influence of C_6H_6 , NO_2 and CO on O_3 concentration were analysed using regression analysis. The results are presented in Figure 2-12 and the results of regression analysis are presented in Table 1-4.

CONCENTRATIONS OF OZONE, BENZENE, NITROZEN DIOXIDE AND CARBON MONOXIDE

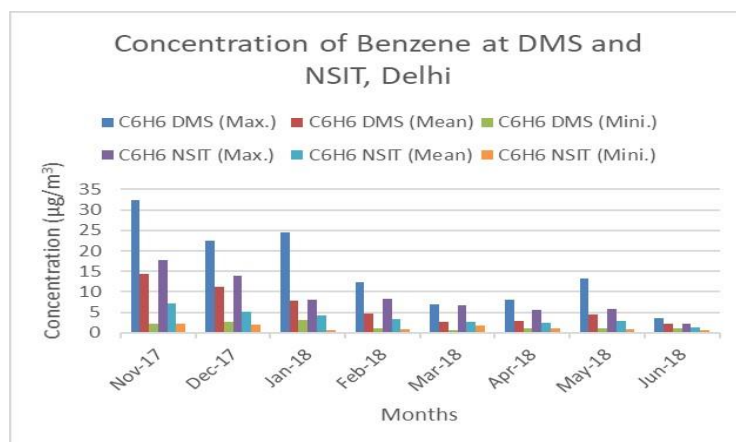


Fig. 2. Concentration of Benzene at DMS and NSIT, Delhi

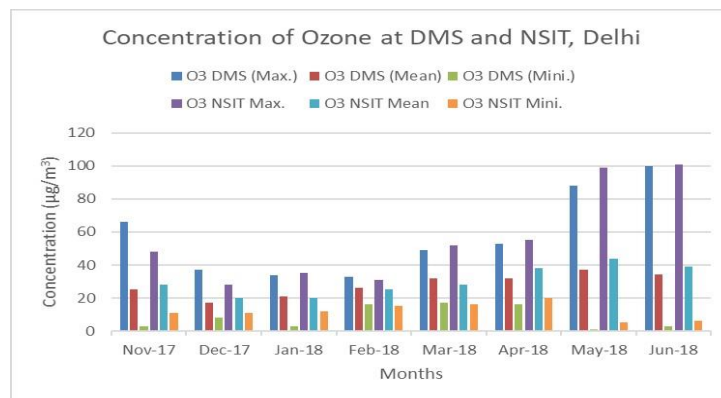


Fig. 3. Concentration of Ozone at DMS and NSIT, Delhi

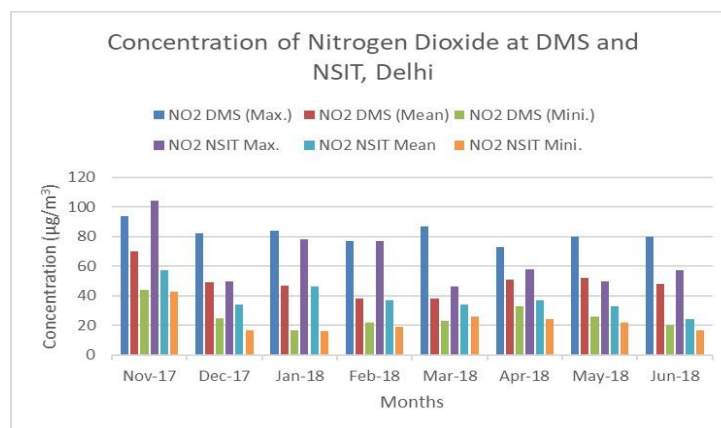


Fig. 4. Concentration of Nitrogen Dioxide at DMS and NSIT, Delhi

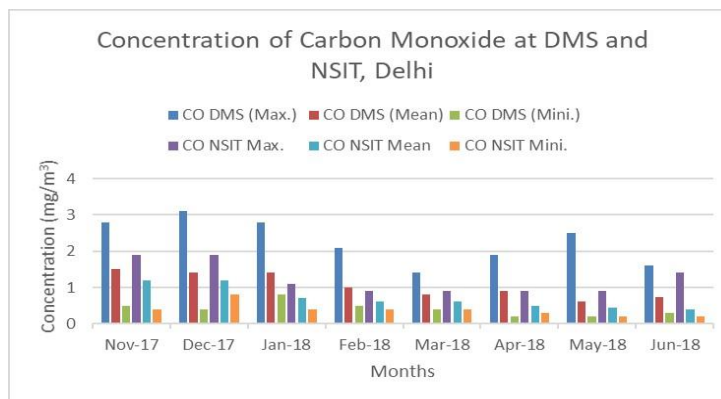


Fig. 5. Concentration of Carbon monoxide at DMS and NSIT, Delhi

It can be seen that the monthly mean concentration of O_3 varies from $17.1\mu\text{g}/\text{m}^3$ to $37.0\mu\text{g}/\text{m}^3$ at DMS site and from $20.0\mu\text{g}/\text{m}^3$ to $44.0\mu\text{g}/\text{m}^3$ at NSIT site. O_3 was observed to be maximum in the month of May (summer) and minimum in the month of December (winter) at both the sites (Moja et al., 2017). The monthly mean concentration of C_6H_6 varies from $2.70\mu\text{g}/\text{m}^3$ to $14.31\mu\text{g}/\text{m}^3$ at DMS site while $1.2\mu\text{g}/\text{m}^3$ to $7.12\mu\text{g}/\text{m}^3$ at NSIT site. C_6H_6 was observed to be maximum in the month of November and minimum in the month of June at both the sites. NO_2 monthly mean concentration varies from $38.0\mu\text{g}/\text{m}^3$ to $70.0\mu\text{g}/\text{m}^3$ at DMS and $24.0\mu\text{g}/\text{m}^3$ to $57.0\mu\text{g}/\text{m}^3$ at NSIT. NO_2 was observed to be maximum in the month of November at both the sites while minimum in the month of March at DMS and in the month of June at NSIT site. The mean seasonal concentrations of O_3 , C_6H_6 , NO_2 and CO are presented in Table 1.

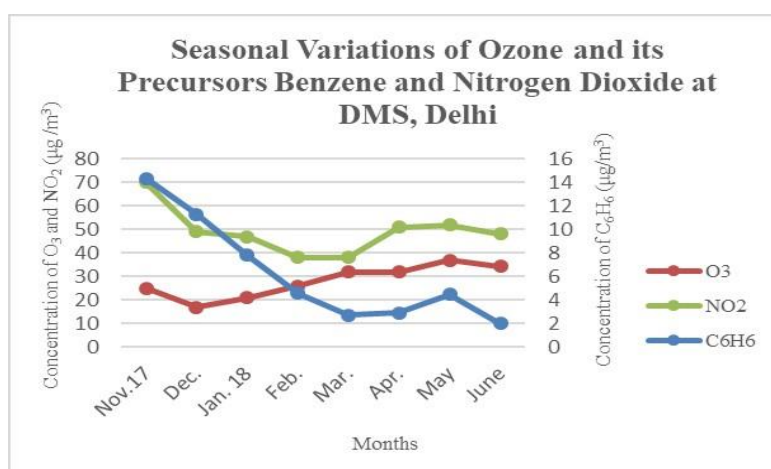
Table 1. The mean Seasonal Concentrations of O₃, C₆H₆, NO₂ and CO at DMS and NSIT sites, Delhi

Monitoring sites	Season	Mean Seasonal Concentrations			
		O ₃ (µg/m ³)	C ₆ H ₆ (µg/m ³)	NO ₂ (µg/m ³)	CO(mg/m ³)
DMS	Winter	21.000 ± 4.000	11.137 ±3.258	55.333 ±12.741	1.433 ±0.058
	Summer	34.443 ± 2.503	3.167 ±1.222	50.333 ±2.082	0.743 ±0.151
NSIT	Winter	22.667 ± 4.619	5.543 ±1.441	44.667 ±10.066	1.033 ±0.287
	Summer	40.333 ± 3.215	2.233 ±0.929	31.333 ±6.658	0.443 ±0.051

The observed increase in winter time NO₂ level is a local manifestation of seasonal variation in vertical mixing intensity that is weaker due to lower planetary boundary layer height (478.03 – 685.92 m), slowest chemical loss due to lowest temperature (15.3 – 21.42°C), much higher anthropogenic emission and associated atmospheric residence times of pollutants in the lower troposphere (Berezina et al., 2020, Venkanna, et al.,2015, Monks et al.,2015, Sharma & Sharma 2016). The observed low value of NO₂ in summer can be attributed to stronger vertical mixing due to higher planetary boundary layer height (707.25m – 749.57m) and faster transition from NO₂ to O₃ due to higher temperature (Sharma & Sharma, 2017).

CO monthly mean concentration varies from 0.6 mg/m³ to 1.4mg/m³ at DMS and 0.4mg/m³ to 1.2mg/m³ at NSIT. CO was observed to be maximum in the month of December at both the sites while minimum in the month of May at DMS and in the month of June at NSIT site. C₆H₆ shows the decreasing trend from winter to summer while O₃ shows the increasing trend. NO₂ and CO shows more or less similar trend as C₆H₆. Also, the monthly mean concentration of C₆H₆, NO₂ and CO were found to be higher at DMS site than at NSIT site, probably because DMS is located in a mixed region having industrial, commercial and residential activities, the major residential and commercial areas of Delhi like Janakpuri and Tilak Nagar are located in this district which may be the source of these precursor gases while NSIT site is located in Dwarka, which is being developed as residential green area and a smart city under Delhi Development Authority's 'smart sub-city' project.

Higher concentrations values of C₆H₆ during winter season at both the locations may be due to low rate of dispersion because of the stable atmosphere during the winter season, low rate of degradation and low mixing height (478.03 – 685.92 m) at low temperature (15.3 – 21.42°C) in winter season and reduction in C₆H₆ removal due to slow down of photochemical reactions as a result of short day length and lower solar intensity.

**Fig. 6.** Seasonal variation of Ozone, Benzene and Nitrogen Dioxide at DMS, Delhi

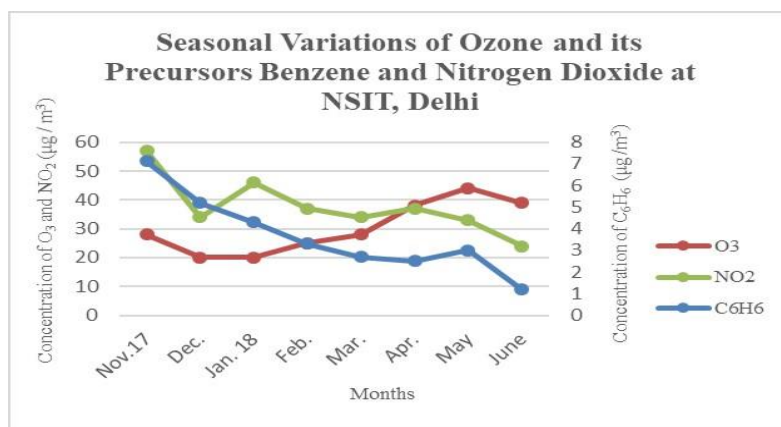


Fig. 7. Seasonal variation of Ozone, Benzene and Nitrogen Dioxide at NSIT, Delhi

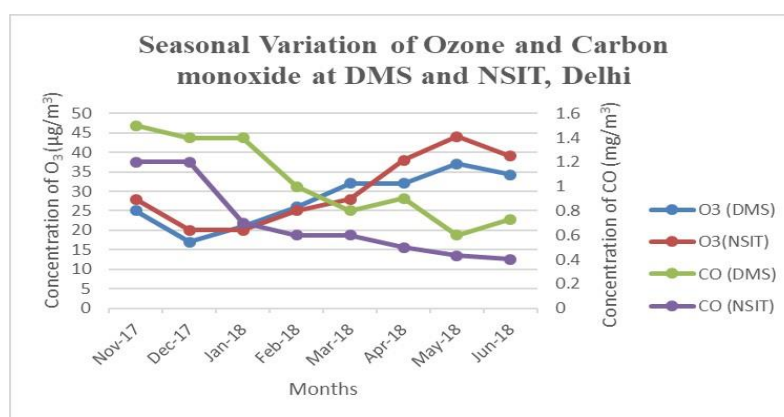


Fig. 8. Seasonal variations of Ozone and Carbon monoxide at DMS and NSIT, Delhi.

C₆H₆ exhibit very clear seasonal characteristics for the study area (Fig. 6). Observed seasonal trends can be addressed by the seasonal characteristics of the prevailing meteorology, variations in the source strength and, most importantly, the availability of OH radical and insolation that take care of the removal process of the VOC species from the atmosphere. The meteorology in Delhi shows an explicit winter and summer characteristics. In the winter months' calm conditions and high stability of the atmosphere prevails, which hinder the pollutants from dissipating faster. Temperature inversion, which is a common phenomenon in the winter months and low mixing heights do restrict dilution process of the pollutants. Thus in the winter months the pollutants generally show a higher level of concentration. In contrast, the summer months, the study area experience higher mixing height (707.25 – 749.57 m) and an unstable atmosphere. Meteorologically these factors favour to better mixing and easy dissipation of the pollutants leading to their lower levels in the atmosphere. Delhi records more insolation during summers which helps in the photolysis of species like ozone, aldehydes etc., and leading to the formation of OH radical. Thus in the summer months high level of OH concentration could prevail in the atmosphere of Delhi, which plays the key role in the atmospheric clean up and degradation process of the aromatic VOCs. The seasonal profiles were almost similar at both the sites. The transition in variability of O₃, C₆H₆, NO₂ and CO can be easily seen with the change of season from winter to summer (Fig. 6, 7 & 8). Also in order to infer the effect of precursors on concentration of O₃, the O₃-C₆H₆, O₃-NO₂ and O₃-CO ratio has been calculated and plotted for period of study (Fig. 9, 10 & 11). It has been found that these ratio shows the similar trend at both the sites but the values are higher at NSIT than DMS site, indicating that the precursors do effect the concentrations of O₃.

The efficiency of O_3 photo chemical production depends on the relationship between C_6H_6 and NO_2 , with an increase in the C_6H_6/NO_2 causing an increase in O_3 production per NO_2 molecule & vice versa and, consequently to an increase in O_3 ground level concentration (Sillman, S. 1999). This feature has been observed in the present study at both the sites in summer(Fig.12).

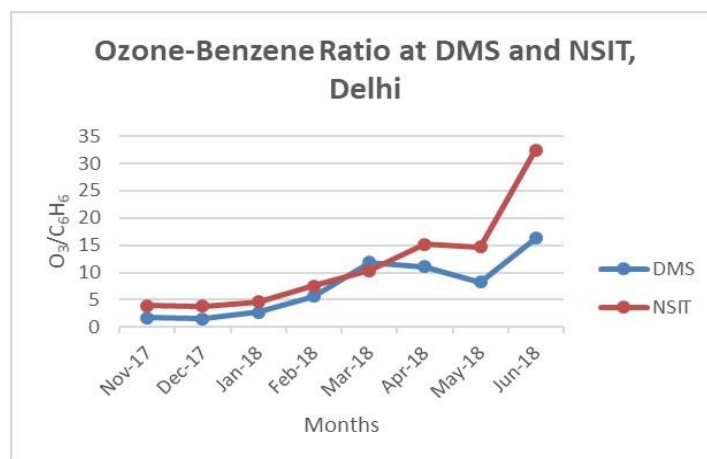


Fig. 9. Ozone-Benzene ratio at DMS and NSIT, Delhi

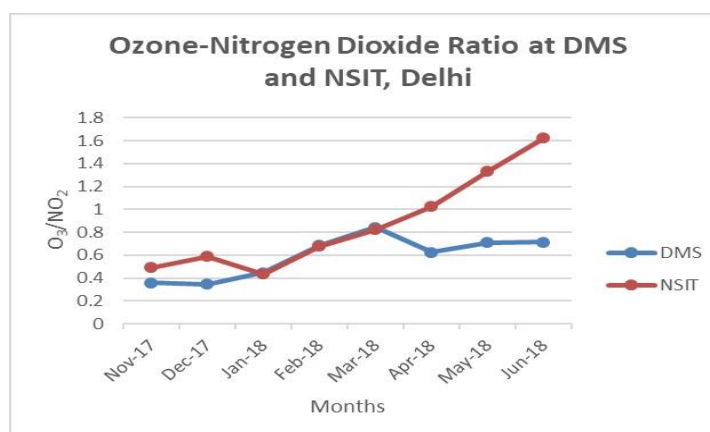


Fig. 10. Ozone-Nitrogen Dioxide ratios at DMS and NSIT, Delhi

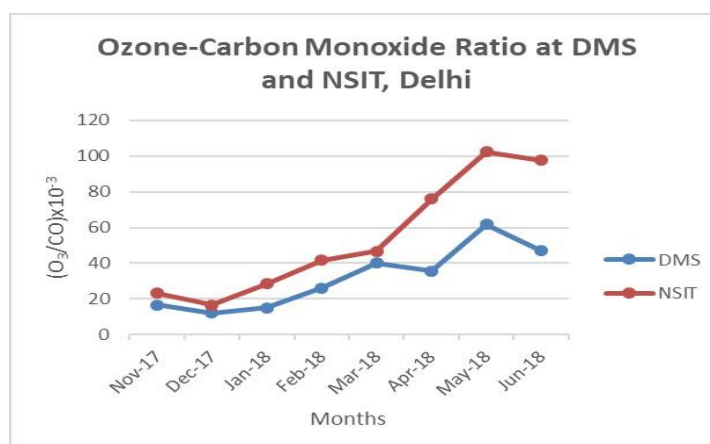


Fig. 11. Ozone-Carbon monoxide ratios at DMS and NSIT, Delhi

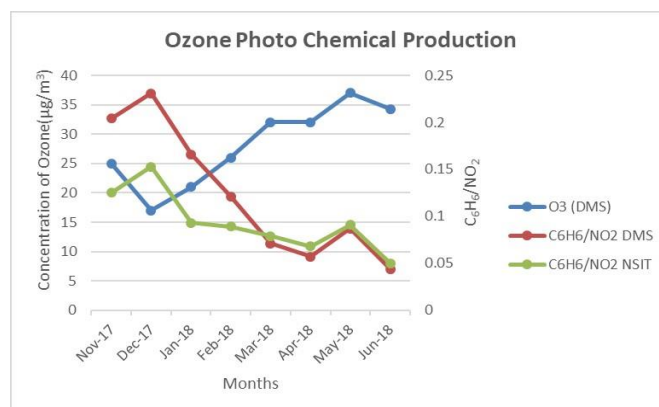


Fig. 12. Ozone Photo Chemical Production

CORRELATION OF OZONE WITH ITS PRECURSORS BENZENE, NITROZEN DIOXIDE AND CARBON MONOXIDE AND SOME METEOROLOGICAL VARIABLES

linear Regression analysis was carried out in order to determine relations among the measured variables. The Regression analysis results are given in Table 2 and 3 for both sampling sites.

Table 2. Correlation of O₃ with C₆H₆, NO₂ and CO during summer and winter

Monitoring sites	Pollutant	Season	C ₆ H ₆	NO ₂	CO
			r ²	r ²	r ²
DMS	O ₃	Winter	0.213	0.679	0.750
		Summer	0.475	0.081	0.985
NSIT	O ₃	Winter	0.902	0.728	0.250
		Summer	0.356	0.004	0.139

Table 3. Correlation of C₆H₆ with NO₂ and CO during summer and winter

Monitoring sites	Pollutant	Season	NO ₂	CO
			r ²	r ²
DMS	C ₆ H ₆	Winter	0.779	0.711
		Summer	0.794	0.354
NSIT	C ₆ H ₆	Winter	0.419	0.559
		Summer	0.702	0.271

O₃ had positive correlation with C₆H₆, NO₂ and CO during winter at both the sites but this correlation is found to be weak at DMS (r²=0.213) than NSIT (r²=0.902) for C₆H₆ and found to be strong at DMS (r²=0.750) than NSIT (r²=0.250) for CO. With NO₂, the correlation was found to be strong at both the sites (r²=0.679 at DMS and r²=0.728 at NSIT). In summer, the correlation was found to be weak in comparison to winter. CO shows strong negative correlation with O₃ at DMS (r²=0.985) but weak correlation at NSIT (r²=0.139) while NO₂ shows weak correlation with O₃ at DMS (r²=0.062) but very weak or no correlation at NSIT (r²=0.004). With C₆H₆, the correlation was found to be moderate at both the sites (r²=0.475 at DMS and r²=0.356 at NSIT). When O₃ precursors are mutually correlated (Table 3), it was found that, C₆H₆ is strongly correlated with NO₂ both in winter and summer at both the sites but correlation is stronger in summer than is winter, while correlation of CO with C₆H₆ is stronger in winter than in summer.

INFLUENCE OF TEMPERATURE, RELATIVE HUMIDITY AND WIND SPEED ON CONCENTRATION OF OZONE AND ITS PRECURSORS, BENZENE, NITROZEN DIOXIDE AND CARBON MONOXIDE

The influence of Temperature, Relative Humidity and Wind Speed on concentration of O₃ and its precursors Benzene, Nitrogen Dioxide and Carbon-monoxide has been studied using regression analysis and the results are presented in Table 4.

Table 4. Correlation of O₃, C₆H₆, NO₂ and CO with Meteorological Variables Temperature, Relative Humidity and Wind Speed during summer and winter

Monitoring sites	Pollutant	Season	Temperature	Relative Humidity	Wind Speed	Reference	
			r ²	r ²	r ²		
DMS	O ₃	Winter	0.375	0.025	0.395	Sharma, 2020 Sharma, 2020	
		Summer	0.939	0.027	0.071		
	C ₆ H ₆	Winter	0.968	0.901	0.961		
		Summer	0.239	0.686	0.778		
	NO ₂	Winter	0.814	0.477	0.918		
		Summer	0.002	0.985	0.998		
	CO	Winter	0.856	0.399	0.871		
		Summer	0.984	0.002	0.021		
	NSIT	O ₃	Winter	0.864	0.439		0.041
			Summer	0.708	0.218		0.311
C ₆ H ₆		Winter	0.995	0.709	0.997		
		Summer	0.005	0.976	0.997		
NO ₂		Winter	0.114	0.021	0.414		
		Summer	0.236	0.831	0.746		
CO		Winter	0.625	0.974	0.605		
		Summer	0.665	0.417	0.316		

The meteorological variables under study that influence the concentration of O₃ are the temperature, relative humidity and wind speed. There is good correlation of O₃ with temperature ($r=0.612$, $r^2=0.375$) and wind speed ($r=-0.629$, $r^2=0.395$) which is followed by relative humidity ($r=-0.159$, $r^2=0.025$) in winter. Thus in winter the high concentration of O₃ are therefore, likely to occur with high temperature and low relative humidity. In summer, there is strong correlation of O₃ with temperature ($r=0.969$, $r^2=0.939$) but very weak correlation with relative humidity ($r=-0.169$, $r^2=0.027$) and win speed ($r=-0.267$, $r^2=0.071$). Thus in summer, the high concentration of O₃ are therefore likely to occur with high temperature, low relative humidity and low wind speed (Saini et al, 2008, Sharma et al., 2016).

As O₃ precursor C₆H₆, NO₂ and CO are concerned, there is strong correlation of C₆H₆ with temperature, relative humidity and wind speed but this correlation is positive with temperature and negative with relative humidity and wind speed at both the sites in winter. Similar correlation has been observed in case of NO₂ and CO in winter. However, these correlations are relatively weaker in summer. This indicate that the precursors C₆H₆, NO₂ and CO influence the concentration of O₃ through meteorological variables temperature, relative humidity and wind speed. Also the correlation of O₃ and its precursors C₆H₆, NO₂ and CO with meteorological variables are found to be relatively weaker at NSIT site than DMS site. It may be due to the complex sources of these pollutants at DMS site which is industrial, commercial and residential site than at NSIT site which is purely residential site developed as a green region.

A comparison of our study with other studies related to Ozone and its precursors is given in Table 5.

Table 5. Comparison of Our study with other studies

Study	City/ Country	Study Area	Pollutants with level	Findings
Lal S. et al., 2000	Ahmedabad, India	Urban	O ₃ and its Precursors NO _x , CO & CH ₄ . O ₃ (24±4 - 60±6 µg/m ³)	Ozone concentrations are observed to be maximum during autumn and winter months due to higher amounts of precursor gases.
Kleinman, L.I., 2005.	U.S.	Urban	O ₃ and its precursors NO _x and VOCs. O ₃ production rate (0-310) µg/m ³ /h	Conditions for O ₃ production vary from strongly NO _x limited to strongly VOC limited.
Beig G et al., 2007.	India	Urban	O ₃ and its precursors NO _x and CO O ₃ ; Max. 170-180 µg/m ³ , Mini. 20-30 µg/m ³	Precursors plays significant role to photo-chemically produce ozone. Local emissions and their temporal variation due to prevailing meteorological condition are the responsible factors.
Saini, R. et al., 2008.	Agra, India	Urban	O ₃ and its precursors NO ₂ and CO O ₃ (average conc):2.4 - 138 µg/m ³ .	The high concentration of O ₃ at SJC is due to higher abundance of precursors NO ₂ and CO.
Sierra, A. et al., 2013.	Maxico city, Maxico	Urban Maxico.	O ₃ sensitivity to its precursors. O ₃ ; maximum reduction rate of 0.4 µg/m ³ /1% reduction in VOC emissions	VOC controls would have a better effect on ambient air O ₃ reduction.
Nishanth T. et al., 2014	Kannur, India	Rural coastal (non-industrial)	O ₃ , NO _x , CH ₄ , & total NHMCs O ₃ , Max. 101.66 µg/m ³ , Mini. 31.52 µg/m ³	The net effect of NO _x on O ₃ concentration was negative with a decaying exponential correlation indicating a possible VOC sensitive location.
Motesaddi Zarandi et al. 2015.	Tehran, Iran	Urban	NO _x & Surface O ₃ concentration Daily Variation: O ₃ ; Mini.14.12 µg/m ³ Max. 132.52 µg/m ³ . NO _x : Mini. 56.27 µg/m ³ , Max. 151.36 µg/m ³ ,	Factors for O ₃ trend: Job shifts, solar radiation and photochemical reactions are the main causes of daily changes for these pollutants; in case of long-term trend of NO ₂ .
Sharma Ashima et al., 2016	Delhi, India	Urban, Industrial, Commercial & residential	O ₃ , NO ₂ , NO, CO, CH ₄ , NMHCs. O ₃ (Annual average) 60±12 µg/m ³ NO ₂ :28.2±7.52 µg/m ³ , CO:2.25±0.6 mg/m ³	The mixing ratio of surface O ₃ positively correlate with NO ₂ , TNMHCs, NO ₂ /NO and NMHCs/NO, and influence the surface O ₃ production.
Kinga Walaszek et al.,2017	Poland	Urban	O ₃ , NO _x , VOCs. O ₃ ; 56 - 102µg/m ³	Mixed sensitivity to emissions of precursors
Sharma R, Sharma N. 2017	Gurgaon, Rohtak & Panchkula,Haryana, India	Urban	O ₃ , SO ₂ , NO, NO ₂ , CO O ₃ : 17.5-31.5 µg/m ³	Seasonal effects plays significant role in regulating the concentration of O ₃ , NO _x , CO and SO ₂ .
Garg A. et al., 2018	Delhi, India	Urban	C ₆ H ₆ , BTP-X Dwarks: 0.5 – 6.66µg/m ³ Sadipur:1.1 – 12.71 µg/m ³	The concentration of BTP-X was found higher during winter season as compare to the summer season.
TING TING QIN et al., 2021	Baicheng Region, China	Urban	O ₃ and Its precursor variability. O ₃ : 17 - 213 µg/m ³ Average: 83 µg/m ³	Overall O ₃ concentration follow as: spring > summer > winter > autumn in 2018. The situation in 2018 was related to the O ₃ precursor and other meteorological factors.
Present Study, 2021	Delhi, India	Urban (Industrial, Commercial and Residential)	O ₃ and its precursors C ₆ H ₆ , NO ₂ , CO & meteorological variables. Average O ₃ : DMS, 3.167 – 11.137 µg/m ³ , NSIT; 2.233 – 5.543 µg/m ³	The natural and anthropogenic sources of the study area contribute significantly in regulating the concentration of O ₃ and its precursors.

CONCLUSIONS

Following conclusion can be drawn from the present study

1. The monthly mean concentration of C_6H_6 , NO_2 and CO are higher at DMS site than at NSIT site while the monthly mean concentration of O_3 is higher at NSIT site than at DMS site. This indicate that the natural and anthropogenic sources of the study area contribute significantly in regulating the concentration of O_3 and its precursors.
2. The O_3 and its precursors exhibits seasonal characteristics. A sharp transition has been observed in variability as the season changes from winter to summer.
3. Seasonal effects play significant role in regulating the concentration of O_3 and its precursors C_6H_6 , NO_2 and CO .
4. In order to infer the effect of precursors on concentration of O_3 , $O_3-C_6H_6$, O_3-NO_2 and O_3-CO ratio has been calculated and plotted for period of study (Fig. 9, 10, 11). It has been found that these ratio shows the similar trend at both the sites but the values are higher at NSIT than DMS site, indicating that the concentrations of precursors do effect the concentration of O_3 .
5. Regression analysis reveal that C_6H_6 , NO_2 and CO play significant role in formation and destruction of O_3 . It is also effected by prevailing meteorological conditions of the study area.
6. Increase in the C_6H_6/NO_2 ratio caused an increase in O_3 production and vice versa, of the NO_2 molecule and, consequently, to an increase (or decrease) in ground-level O_3 concentration. This feature has been observed during summer in the present study.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been thoroughly observed by the authors

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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REFERENCES

- Ainsworth, E.A., Yendrek, C.R., Sitch, S., Collins, W.J. and Emberson, L.D. (2012) The Effects of Tropospheric Ozone on Net Primary Productivity and Implications for Climate Change. *Annu. Rev. Plant Biol.* 63; 637–661.
- Beig G., Gunthe S., Jadhav D.B. (2007), Simultaneous measurement of Ozone and its precursors on a diurnal scale at a semi-urban site in India, *J. Atmos. Chem.*, 57, 239-253, DOI: 10.1007/s 10874-007-9068-8.
- Barletta, B., Meinardi, S., Rowland, F. S., Chan, C. Y., Wang, X. M., Zou, S. C., Chan, L. Y., and Blake, D. R. (2005). Volatile organic compounds in 43 Chinese cities, *Atmos. Environ.*, 39; 5979–5990.
- Berezina, E., Moiseenko, K., Skorikhod, 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* 11, 1262; doi: 10.3390/atmos 11111262.
- Chang, C.Y., Faust, E., Hou, X., Lee, P., Kim, H.C., Hedquist, B.C., Liao, K.J., (2016) Investigating ambient ozone formation regimes in neighboring cities of shale plays in the Northeast United States using photochemical modeling and satellite retrievals. *Atmos. Environ.* 142, 152–170.
- Chaudhary, S. and Kumar, A. (2012). Monitoring of benzene, toluene, ethylbenzene and xylene (BTEX) concentrations in ambient air in Firozabad, India, *Int. Arch. Appl. Sci. Technol.*, 3; 92–96.
- Chou, C.C.K., Tsai, C.Y., Chang, C.C., Lin, P.H., Liu, S.C. and Zhu, T. (2011). Photochemical production of ozone in Beijing during the 2008 Olympic Games. *Atmos. Chem. Phys.*, 11; 9825–9837.
- Civan, M. Y., Kuntasal, O. O., and Tuncel, G. (2011). Source apportionment of ambient volatile organic compounds in Bursa, a heavily industrialized city in turkey, *Environ. Forensics*, 12; 357–370.
- Faridi, S., Shamsipour, M., Krzyzanowski, M., Kunzli, N., Amini, H. and co-authors. (2018). Long-term trends and health impact of PM_{2.5} and O₃ in Tehran, Iran, 2006-2015. *Environ. Int.* 114, 37–49. doi:10.1016/j.envint.2018.02.026
- García, M.A., Sanchez, M.L., Perez, I.A., de Torre, B. (2005) Ground level ozone concentrations at a rural location in northern Spain. *Sci Total Environ* ;348: 135-50.
- Garg, A.1., Gupta, N.C.1, and Tyagi, S.K. (2019). Study of Seasonal and Spatial Variability among Benzene, Toluene, and p-Xylene (BTp-X) in Ambient Air of Delhi, India, *Pollution*, 5(1): 135-146
- Geng, F., Tie, X., Xu, J., Zhou, G., Peng, L., Gao, W., Tang, X. and Zhao, C. (2008). Characterizations of ozone, NO_x, and VOCs measured in Shanghai, China. *Atmos. Environ.* 42; 6873–6883.
- Goldberg, D.L., Vinciguerra, T.P., Anderson, D.C., Hembeck, L., Cauty, T.P., Ehrman, S.H., Martins, D.K., Stauffer, R.M., Thompson, A.M., Salawitch, R.J., (2016). Ozone Source Attribution in the Eastern United States using Guidance from Observations during DISCOVER-AQ Maryland. *Geophys. Res. Lett.*, 43, 2249–2258.
- Jerrett, M, Burnett, R.T., Pope, C.A., Ito K., Thurston, G., Krewski, D. (2009) Long-term ozone exposure and mortality. *New Engl J Med.*;360:1085-95.
- Karl, T., Graus, M., Striednig, M., Lamprecht, C., Hammerle, A., Wohlfahrt, G., Held, A., Von Der Heyden, L., Deventer, M.J., Krismer, A., (2017). Urban eddy covariance measurements reveal significant missing NO_x emissions in Central Europe. *Sci. Rep.*, 7, 1–9.
- Keymeulen, R., Gögényi, M., Héberger, K., Priksane, A., and Lagenhove. H. V. (2001). Benzene, toluene, ethylbenzene and xylenes in ambient air and Pinussylvestris L. needles: A comparative study between Belgium, Hungary and Latvia, *Atmos. Environ.*, 35; 6327–6335.
- Kleinman L.I. (2005) The dependence of Tropospheric Ozone Production rate on Ozone Precursors, *Atmospheric Environment*, 39, 3, 575-586.
- Lal S., Naja M, Subbaraya B.H.,(2000) Seasonal Variations in Surface Ozone and its precursors over an urban site in India, *Atmospheric Environment*,34, 17, 2713-2724.

- Mazzuca, G.M., Ren X., Loughner, C.P., Estes, M., Crawford, J.H., Pickering, K.E., Weinheimer, A.J., Dickerson, R.R. (2016). Ozone production and its sensitivity to NO_x and VOCs: Results from the DISCOVER-AQ field experiment, Houston 2013. *Atmos. Chem. Phys. Discuss.* 16, 14463–14474. *Atmosphere*, 11, 1262 14 of 16
- Miller, L., Xu, X. H., Wheeler, A., Atari, D. O., GrgicakMannion, A., and Luginaah, I. (2011). Spatial Variability and Application of Ratios between BTEX in Two Canadian Cities, *The Scientific World Journal*, 11;2536–2549.
- Mittal, M.L., Hess, P.G., Jain, S.L., Arya, B.C., Sharma, C. (2007). Surface Ozone in the Indian Region, *Atmospheric Environment*, Vol. 41, Issue 31, 6572-6584.
- Moja, S.J., and Thivhafuni, P. (2017), NO₂, SO₂, C₆H₆, O₃ and PM₁₀ levels within the BA-Phalabonwa Municipality of South Africa, *Air Pollution XXV, WIT Transection on Ecology and the Environment*, Vol. 211 ISSN: 1746-448X (On line), doi 102495 AIR 170101.
- Monks, P.S., Archibald, A.T., Colette, A., Cooper, O., Coyle, M., Derwent, R., Fowler, D., Granier, C., Law, K.S., Mills, G.E. (2015) Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer. *Atmos. Chem. Phys.*, 15, 8889–8973.
- Motesaddi Z., Alimohammadi M., Moghaddem V.K., Hasanvand M.S., Miranzadeh M.B., Rabbani D., Mostafaii G.R., Sarsangi V., Hajiketabi S., Tehrani A.M. (2015), *Journal of Environmental Health, Science and Technology*, 13, 63, DOI: 10.1186/s40201-015-0218-7.
- National Research Council (1991). *Rethinking the Ozone Problem in Urban and Regional Air Pollution*; The National Academies Press: Washington, DC, USA.
- Nishanth, T, Praseed, K.M., Kumar, M.K.S., Valsaraj, K.T. (2014) Influence of ozone precursors and PM₁₀ on the variation of surface O₃ over Kannur, India. *Atmos Res* ;138:112-24.
- Parra, M. A., González, L., Elustondo, D., Garrigó, J., Bermejo, R., and Santamaría, J. M. (2006). Spatial and temporal trends of volatile organic compounds (VOC) in a rural area of Northern Spain, *Sci. Total Environ.*, 370; 157–67.
- Pires, J.C.M. (2012). Ozone Weekend Effect Analysis in Three European Urban Areas. *CLEAN—Soil, Air, Water*, 40; 790–797
- Pusede, S.E. and Cohen, R.C. (2012). On the observed response of ozone to NO_x and VOC reactivity reductions in San Joaquin Valley California 1995–present. *Atmos. Chem. Phys.* 12; 8323–8339.
- QIN T., Wang J., Li R., Fang C., (2021), Diurnal and Inter-annual variability of surface ozone in Baicheng region, China, *Tellus B: Chemical and Physical Meteorology*, 73, 1 DOI: org/10.1080/16000889.2021.1894879.
- Reeves, C. E., Penkett, S. A., Bauguitte, S., Law, K. S., Evans, M. J., Bandy, B. J., Monks, P. S., Edwards, G. D., Phillips, G. (2002). "Potential for photochemical ozone formation in the troposphere over the North Atlantic as derived from aircraft observations during ACSOE". *Journal of Geophysical Research: Atmospheres*. **107** (D23): ACH 14–1–ACH 14–Bibcode:JGRD..107.4707R . doi:10.1029/2002j d002415. ISSN 0148-0227.
- Saini, R., Satsangi, G.S., and Taneja, A. (2008). Concentration of Surface O₃, NO₂ and CO during winter seasons at a semi-arid region, Agra, India, *Indian Journal of Radio and Space Physics*, Vol.37(2),121-130.
- Sharma, A., Sharma, S.K., Rohtash, Mandal, T.K. (2016). Influence of ozone precursors and particulate matter on the variation of surface ozone at an urban site of Delhi, India. *Sustain. Environ. Res.*, 26, 76–83.
- Sharma, R C. (2020). Investigation of Variability of Some Gaseous and Particulate Pollutants over Delhi, Northern India (28°40'N, 76°50'E), *Asian Journal of Water Environment and Pollution*, 17 (3);101-109.
- Sharma, R.C., and Sharma, N. (2016) Influence of some meteorological variables on PM₁₀ and NO_x in Gurgaon, Northern India, *American Journal of Environmental Protection*, Vol. 4, No. 1, 1-6, doi:10.12691/env-4-1-1.
- Sharma, R.C., and Sharma, N. (2017) Influence of Oxides of Nitrogen, Carbon monoxide and Sulphur dioxide on surface Ozone level in different Meteorological seasons, in Haryana State, Northern India, *American Journal of Environmental Protection*, Vol. 5, No. 1, 1-8, doi:10.12691/env-5-1-1.

- Shaw, M. D., Lee, J. D., Davison, B., Vaughan, A., Purvis, R. M., Harvey, A., Lewis, A. C., and Hewitt, C. N. (2015) Airborne determination of the temporo-spatial distribution of benzene, toluene, nitrogen oxides and ozone in the boundary layer across Greater London, UK, *Atmos. Chem. Phys.*, 15; 5083–5097.
- Sierra A., Vanoye A. Y., Mendoza A. (2013), Ozone sensitivity to its precursors emission in north-eastern Mexico for summer air pollution episode, *Journal of the Air and Waste Management Association*, 63, 10, 1221-1233.
- Sillman, S. (1999). The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmos. Environ.* 33, 1821–1845.
- Tiwari, V., Hanai, Y., and Masunaga, S. (2010). Ambient levels of volatile organic compounds in the vicinity of petrochemical industrial area of Yokohama, Japan, *Air Qual. Atmos. Health*, 3; 65–75.
- Trail, M., Tsimpidi, A.P., Liu, P., Tsigaridis, K., Rudokas, J., Miller, P., Nenes, A., Hu, Y. and Russell, A.G. (2014). Sensitivity of air quality to potential future climate change and emissions in the United States and major cities. *Atmos. Environ.* 94; 552–563.
- Velasco, E., Lamb, B., Westberg, H., Allwine, E., Sosa, G., ArriagaColina, J. L., Jobson, B. T., Alexander, M. L., Prazeller, P., Knighton, W. B., Rogers, T. M., Grutter, M., Herndon, S. C., Kolb, C. E., Zavala, M., de Foy, B., Volkamer, R., Molina, L. T., and Molina, M. J. (2007). Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 & 2003 field campaigns, *Atmos. Chem. Phys.*, 7; 329–353.
- Venkanna, R., Nikhil, G.N., Shiva Rao, T., Sinha, P.R., Swami, Y.V. (2015). Environmental monitoring of surface ozone and other trace gases over different time scales; chemistry, transport and modelling. *Int. J. Environ. Sci. Technol.* 12, 1749-1758, doi 10.1007/s 13762-014-0537-8.
- Walaszek, K., Kryza, M., and Werner M. (2018), The role of precursor emission on ground level ozone concentration during summer season in Poland, *J. Atmos. Chem.* 75; 181-204.
- Wang, X.K., Lu, W.Z., Wang, W.J., Leung, A.Y.T. (2003) A study of ozone variation trend within area of affecting human health in Hong Kong. *Chemosphere* ;52: 1405-10.

