

# Influence of Oxides of Nitrogen, Carbon Monoxide and Sulphur Dioxide on Surface Ozone Level in Different Meteorological Seasons in Haryana State, Northern India

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**Abstract** Surface Ozone concentrations are valuable indicators of possible health and environmental impacts. Increasing concentration of Tropospheric ozone (O<sub>3</sub>) is a serious air pollution problem faced commonly by the urban people. In the present study ozone (O<sub>3</sub>), Oxides of Nitrogen (NO<sub>x</sub>) Carbon monoxide (CO) and Sulphur dioxide (SO<sub>2</sub>) data were collected for a period of one year (January 01, 2015 to December 31, 2015) at three ambient air quality monitoring stations (Gurgaon now Gurugram, Rohtak and Panchkula) in Haryana state in Northern India. The O<sub>3</sub>, NO<sub>x</sub>, CO, and SO<sub>2</sub> data were collected by Haryana State Pollution Control Board. The concentration of O<sub>3</sub> is correlated with the concentration of NO<sub>x</sub>, CO, and SO<sub>2</sub> in different meteorological seasons. The regression correlation analysis has been performed between NO<sub>x</sub>, CO, SO<sub>2</sub> and O<sub>3</sub> to investigate the relationship between them. It was found that the variation in concentration of NO<sub>x</sub>, CO and SO<sub>2</sub> influenced the changes in the concentration of O<sub>3</sub> in different seasons of the year. The investigation data showed that NO<sub>x</sub>, CO and SO<sub>2</sub> had the important influence on O<sub>3</sub> concentration variations in monsoon session ( $r^2 = -0.256, -0.322, -0.137$  for Gurgaon,  $r^2 = 0.997, -0.829$  and  $0.843$  for Rohtak and  $r^2 = -0.854, -0.829$  and  $0.262$  for Panchkula). The influence of SO<sub>2</sub> on O<sub>3</sub> concentration has been observed to be different from NO<sub>x</sub> and CO. O<sub>3</sub> and NO<sub>x</sub> were observed to be inversely related in most of the seasons ( $r^2 = 0.124, 0.389, -0.256$  and  $-0.694$  in Gurgaon,  $r^2 = -0.797, -0.819, 0.997$  and  $-0.797$  in Rohtak &  $r^2 = 0.971, -0.074, -0.854$  &  $0.784$  in Panchkula for spring, pre-monsoon, monsoon and post monsoon season respectively). The regression equations have been obtained which correlates O<sub>3</sub> with NO<sub>x</sub>, CO and SO<sub>2</sub>.

**Keywords:** ozone, oxides of nitrogen, carbon monoxide, sulphur dioxide, urban ambient air quality, correlation, regression analysis

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## 1. Introduction

Air Pollution is a challenging problem as it would hinder sustainable development all over the globe [1]. The factors responsible for occurrence of air pollution include meteorological factors, earth surface topographic features and released air pollutants from various sources. Meteorological factors such as wind velocity, wind direction, temperature, and relative humidity together with earth surface roughness are effective agents for mixture of air pollutants. The most important role of meteorology is in the dispersion, transformation and removal of air pollutants from atmosphere. The wind speeds determine the amount of dispersion of pollutants while temperature contributes transformation of pollutants in the atmosphere. The topography and solar heating of region surrounding a

particular pollution source affects the concentration. High pollution levels can be expected during fair weather conditions resulting local wind system and strong temperature inversions in cities situated in mountainous region. Air pollution may be classified into two types according to the nature of formation: primary pollutants which are emitted from their sources directly to the atmosphere such as industry, traffic, domestic heating in winter season and secondary pollutants which results from the chemical reaction between the primary pollutants. Examples of primary pollutants are oxides of nitrogen (NO<sub>x</sub>), carbon monoxide (CO) and sulphur dioxide (SO<sub>2</sub>). Examples of secondary pollutants are photochemical oxidants and ozone (O<sub>3</sub>).

Oxides of Nitrogen in the atmosphere originate either from natural processes or anthropogenic activity. In the lower atmosphere, nitric oxide (NO) is converted to nitrogen dioxide (NO<sub>2</sub>) by reaction with proxy-radicals (RO<sub>2</sub>) or O<sub>3</sub>. The NO<sub>2</sub> generated is then undergoes photo

dissociation in the atmosphere and the atomic oxygen released combines with molecular oxygen to form  $O_3$  [2]. The life time of  $NO_x$  ( $NO+NO_2$ ) in the troposphere ranges from less than one day in summer to several days in the absence of active photochemistry.

Carbon monoxide is an important trace gas in the earth's atmosphere, which performs several important roles in the troposphere. There are a variety of sources, both natural and anthropogenic, for ambient CO. Natural sources include oxidation of methane and natural hydrocarbons, ocean emissions, and emissions from vegetation. In rural areas, these are the most dominant sources; therefore, in a remote location, CO is one of the most dominant precursors for photo-chemical ozone production. In urban areas, however anthropogenic sources including fossil fuel combustion, industrial activities, motor vehicles, biomass burning, and oxidation of anthropogenic hydrocarbons, contribute far more to the concentration of CO than natural sources. The lifetime of CO is approximately 1-3 months, representing the slow rate of mixing and the consumption by reaction with OH. In the troposphere, a significant CO background concentration exists based on continuous CO production from the oxidation of methane and its long lifetime [2].

Sulfur dioxide is a major air pollutant and has significant impacts upon human health. Sulfur dioxide emissions are a precursor to acid rain and atmospheric particulates. It influenced  $O_3$  formation. Role of  $SO_2$  in  $O_3$  formation is dependent on  $HO_2$  produced from  $SO_2$  [3]. The utmost anthropogenic sources of  $SO_2$  consequences are from the burning of fossil fuels and from the smelting sulphide ores [4]. Among man made sources fuel combustion, industry and transportation are the main contributors. A significant feature of  $SO_2$  is that, once it is emitted from the atmosphere, it can be converted through complex oxidation reactions in to fine particulate sulphate and removed from the atmosphere by wet or dry deposition [5,6].

Ozone is a major environmental concern because of its adverse impact on human health [7,8] and also because of its impacts on crops and forest ecosystems [9,10]. Tropospheric  $O_3$  may originate by interchange with the stratosphere and/or photochemical production. In the urban atmosphere,  $NO_x$  and volatile organic compounds may either increase or decrease  $O_3$  concentrations.  $O_3$  formation is closely related to meteorological parameters such as temperature, solar radiation, and wind speed [11].

A thorough understanding of the relationship among  $O_3$ ,  $NO_x$ ,  $SO_2$  and CO under various atmospheric conditions is urgently needed to improve our understanding of the

chemical coupling among these pollutants [12,13,14,15,16]. Seasonal variation effects on gaseous pollutants are of great significance to the life span and cycle of any pollutant in the lower atmosphere [17].

In the present study, the levels of air pollutants  $NO_x$ , CO,  $SO_2$  and  $O_3$  were measured at three urban locations (Gurgaon, Rohtak and Panchkula) in Haryana state (Figure 1) for a period of one year from January 01,2015 to December 31, 2015. The concentrations of  $NO_x$ , CO and  $SO_2$  were statistically correlated with concentration of  $O_3$  using regression analysis in spring, pre-monsoon, monsoon and post monsoon seasons. The regression equations have been obtained which correlates  $O_3$  with  $NO_x$ , CO and  $SO_2$ .

## 2. Description of the Study Area

Haryana is the 20<sup>th</sup> state of India that came into being on 1<sup>st</sup> November 1966. It is situated in the North Western region surrounded by Himachal Pradesh from North, Utrakhand from North East, Rajasthan from the South, U.P and Delhi from East and Punjab from North West. Three districts, Gurgaon, Rohtak and Panchkula of Haryana state have been selected for the present study. The brief information's about sampling sites are given in Table 1.



Figure 1. Map of Haryana state showing study area: Gurgaon (now Gurugram), Rohtak and Panchkula

Table 1. Information on Monitoring sites

Monitoring sites	Site Classification	Description
Gurgaon Vikas Sadan	Urban, faster pace of development.	An urban location near to National Highway-8. Industrial units like Hero group, Honda and Maruti Udyog are situated in the district. Faster pace of development and thickly populated. Gurgaon experiences a monsoon-influenced humid subtropical climate
Rohtak, MDU	Urban, Eastern Haryana Plain	Rohtak district constitutes a major part of eastern Haryana plain. The district has witnessed rapid industrialization, urbanization, diversification in agriculture and change in occupation structure. The district is situated on the National Highway No. 10. The climate of Rohtak district is sub-tropical, semi arid, continental and monsoon type.
Panchkula HSPCB, Sector 6	Urban Residential, Himalayas boundary fault zone	Panchkula district has a sub tropical continental monsoon climate having, hot summers, cool winters, good monsoon rainfall. It has great variation in temperature (-1 °C to 43 °C). Sometimes winter frost occurs during December and January. The district lies in the Himalayas boundary fault zones and earthquakes of moderate to high intensity have occurred in the past. Morni hills constitute the highest point of the district as well as of Haryana.

Gurgaon district falls in the southern most region of the state of Haryana. To its advantage of being situated in vicinity of Delhi, Gurgaon falls under National Capital Region. It lies in between the 27° 39' and 28° 32'25'' latitude, and 76° 39' 30'' and 77° 20' 45'' longitude. Gurgaon is the sixth largest city of Haryana State and is situated on both sides of National highway 8. It accommodates a population of 1514432 (2011 Population census figures), 5.97 percent of the state population. Its density according to 2011 population census is 1204 persons per Sq. km. against 573 in the state, which get further compounded due to migration of people from different part of country in search of job. It has been on the faster pace of the development and emerged as the industrial and financial hub of Haryana. Rapid urbanization, increasing industrialization and enhanced men made perturbations added excess pollutants in the atmosphere resulting environmental degradation and climate change [18].

Rohtak district is located in southeastern part of Haryana State (30° 1'N, 75° 17'E) and constitutes a major part of eastern Haryana plain. The climate of Rohtak district is sub-tropical, semi arid, Continental and monsoon type. Thus, it has hot summers, cool winters and small rainy season. Due to less rainfall and its short duration the agricultural activities is mostly dependent upon canal irrigation and Tube wells. According to the 2011 census Rohtak district has a population of 1,058,683[1]. The district has a population density of 607 inhabitants per square kilometer. Its population growth rate over the decade 2001-2011 was 12.61%.The district has witnessed rapid industrialization, urbanization, diversification in agriculture and change in occupation structure. The district is situated on the National Highway No. 10.

Panchkula (30°41' N and 76°52' E) district has a sub tropical continental monsoon climate having, hot summers, cool winters, good monsoon rainfall. It has great variation in temperature (-1 °C to 43 °C). Sometimes winter frost occurs during December and January. The district also receives winter rains from the western disturbance. The rainfall is mostly received in the monsoon. Morni hills constitute the highest point of the district as well as of Haryana. The Ghaggar is the only perennial river, which is very shallow outside of the monsoon. Generally the slope of the district is from north east to south west and in this direction, most of the rivers/streams rain-fed torrents flow down and spread much gravel and pebbles in their beds. The soils in the district are mainly light loam. The district lies in the Himalayas boundary fault zones and earthquakes of moderate to high intensity have occurred in the past. According to 2011 census of India, it was the least populous district of Haryana and had a population of 558890.The district has a population density of 622 inhabitants per square kilometer. Its population growth rate over the decade 2001-2011 was 19.32% [18,19].

### 3. Methods & Materials

For the present study, we used ambient air quality data collected by the Haryana State Pollution Control Board (HSPCB) using Ozone analyzer (O-342M), NOx analyzer

(AC-32M), CO analyzer (CO-12M), and SO<sub>2</sub> analyzer (AF-22M) [20] for a period of one year from January 01, 2015 to December 31, 2015. The NO<sub>x</sub>, CO, SO<sub>2</sub> and O<sub>3</sub> samples were collected by the HSPCB using their respective analyzers which could be operated up to 28 hrs and the sampling duration was 24 hrs as accepted by the Environmental Protection Agency (EPA) of the U.S.A. and the Central Pollution Control Board (CPCB) of India. Oxides of nitrogen analyzer use proven chemi-luminescence technology to measure NO<sub>x</sub> in ambient air quality. The CO analyzer works on the principle of non-dispersive absorption and SO<sub>2</sub> analyzer operates on the principle of light absorption, where the SO<sub>2</sub> molecules are excited by absorbing light at one wavelength and later decay to a lower energy state by emitting UV light at a different wavelength which is proportional to SO<sub>2</sub> concentration. The O<sub>3</sub> analyzer also works on the absorption principle i.e. O<sub>3</sub> molecules absorbs UV light at 254nm wavelength. The degree of absorption is directly related to O<sub>3</sub> concentration as described by Beer-Lambert law [21,22,23]. O<sub>3</sub> measurements are automatically corrected for gas temperature / pressure changes and can be displayed in units of ppm, µg/m<sup>3</sup> or mg/m<sup>3</sup>. In this study the regression correlation analysis has been performed between O<sub>3</sub> & NO<sub>x</sub>, CO and SO<sub>2</sub> for different meteorological seasons to investigate the relationships between them. This analysis will give an idea about which season and meteorological conditions play a major role in regulating O<sub>3</sub>, CO, SO<sub>2</sub> and NO<sub>x</sub> concentrations over the sampling sites and also how SO<sub>2</sub>, NO<sub>x</sub> and CO concentration affects O<sub>3</sub> under different meteorological conditions.

## 4. Results and Discussion

In this study, we have analyzed and correlated the NO<sub>x</sub>, CO and SO<sub>2</sub> data with O<sub>3</sub> concentrations obtained at three sites in Haryana State in Northern India for spring, pre-monsoon, monsoon and post-monsoon seasons for the period from January 01, 2015 to December 31, 2015. The NO<sub>x</sub>, CO and SO<sub>2</sub> variations and their influences on concentration of O<sub>3</sub> in the ambient air were analyzed using regression analysis. The graphs are presented in Figure 2- Figure 10 and the results of regression analysis are presented in Table 2 - Table 4. A comparison of coefficient of determination for NO<sub>x</sub>, CO and SO<sub>2</sub> with O<sub>3</sub> at Gurgaon, Rohtak and Panchkula for spring, pre-monsoon, monsoon and post monsoon seasons is presented in Figure 11.

### 4.1. Influence of NO<sub>x</sub>, CO and SO<sub>2</sub> on Concentration of O<sub>3</sub> in Gurgaon

The NO<sub>x</sub>, CO and SO<sub>2</sub> variations and their influences on concentration of O<sub>3</sub> in the ambient air for Gurgaon are presented in Figure 2, Figure 3 & Figure 4 and the results of regression analysis are presented in Table 2.

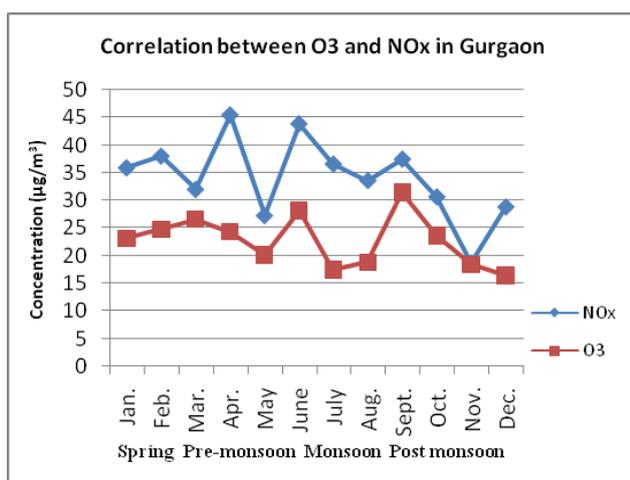
It can be seen that the monthly mean concentration of O<sub>3</sub> was observed to be maximum in the month of September and minimum in the month of July while NO<sub>x</sub>, CO and SO<sub>2</sub> observed to be maximum in the month of April, June and June respectively and minimum in the months of November, September and August respectively. Low O<sub>3</sub> concentration (17.5 µg m<sup>-3</sup> in the month of July)

was observed in monsoon due to the strong winds that dilute air by carrying  $O_3$  precursors away from the site. The observed results of  $O_3$  can be attributed to lower vertical mixing due to lower planetary boundary layer height, stronger titration by  $NO_x$  due to higher emission related to heating and lower photochemical production due to lower temperature and solar radiations. The observed low values of  $NO_x$  can be attributed to stronger vertical mixing due to higher planetary boundary layer height, faster transition from  $NO_x$  to  $O_3$  due to higher temperature and higher wet deposition due to precipitation [24]. The observed winter increase of  $NO_x$  may be

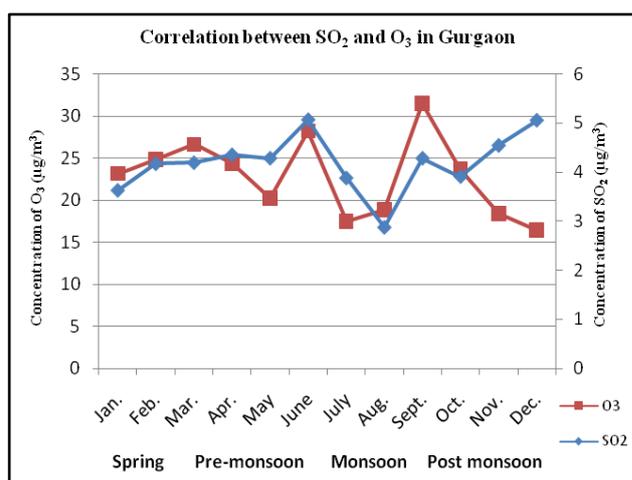
attributed to weaker vertical mixing due to particularly low planetary boundary layer height, slowest chemical loss due to the lowest temperature, solar radiation and oxidant concentration and particularly much higher anthropogenic emission in winter [25,26]. Since Gurgaon is on faster pace of development and thickly populated and so this area has an envelope of dust and pollutants gases which in turn slow down photo oxidation of  $NO_x$ . The observed peak in CO and  $SO_2$  in pre-monsoon season may be due to enhanced incomplete combustion of fuels, enhanced vehicular emission and chemical transformation of interacting gases in dry season [27].

**Table 2. Correlation coefficient and the regression equation between  $NO_x$ , CO,  $SO_2$  and  $O_3$  in Gurgaon**

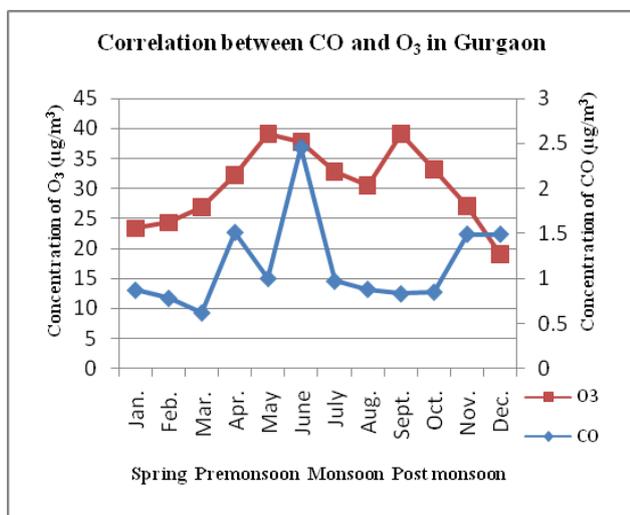
Season (Gurgaon)	$NO_x$ Range (Monthly mean) ( $\mu g/m^3$ )	$r^2$	$O_3$ Equation	CO Range ( $mg/m^3$ )	$r^2$	$O_3$ Equation	$SO_2$ range ( $\mu g/m^3$ )	$r^2$	$O_3$ Equation
Spring	31.99-37.99	-0.124	$O_3 = -0.378 NO_x + 38.153$	0.62-0.87	0.980	$O_3 = -0.014 CO + 0.035$	3.63-4.19	0.506	$O_3 = 4.7401 SO_2 + 5.8921$
Pre-monsoon	27.28-45.42	0.389	$O_3 = 0.331 NO_x + 11.388$	1.00-2.45	-0.999	$O_3 = -6.4 \times 10^{-5} CO + 0.036$	4.28-5.06	0.605	$O_3 = 4.7401 SO_2 + 5.8921$
Monsoon	33.6-37.45	-0.256	$O_3 = 2.329 NO_x - 60.945$	0.83-0.97	-0.322	$O_3 = -0.036 CO + 0.067$	2.88-4.38	-0.137	$O_3 = 4.7401 SO_2 + 5.8921$
Post monsoon	18.73-30.67	-0.694	$O_3 = 0.229 NO_x + 13.530$	0.85-1.49	0.356	$O_3 = -0.016 CO + 0.046$	3.91-5.05	0.922	$O_3 = 4.7401 SO_2 + 5.8921$



**Figure 2.** Correlations between  $NO_x$  and  $O_3$  in Gurgaon



**Figure 4.** Correlations between  $SO_2$  and  $O_3$  in Gurgaon



**Figure 3.** Correlations between CO and  $O_3$  in Gurgaon

Regression analysis reveals that  $O_3$  is negatively correlated with  $NO_x$  in spring ( $r^2 = -0.124$ ), monsoon ( $r^2 = -0.256$ ) and Post monsoon seasons ( $r^2 = -0.694$ ) and positively correlated during pre-monsoon season ( $r^2 = 0.389$ ) [23]. CO showed negative correlation with  $O_3$  during pre-monsoon ( $r^2 = -0.999$ ) and monsoon ( $r^2 = -0.322$ ) seasons and positive correlation during spring ( $r^2 = 0.980$ ) and post monsoon ( $r^2 = 0.356$ ) seasons.  $SO_2$  showed weak negative correlation with  $O_3$  in monsoon ( $r^2 = -0.137$ ) season and positive correlation during spring ( $r^2 = 0.506$ ), pre-monsoon ( $r^2 = 0.605$ ) and post monsoon ( $r^2 = 0.922$ ) seasons. It can be seen that during monsoon season,  $NO_x$ , CO and  $SO_2$  showed weak negative correlation with  $O_3$  in Gurgaon [28]. During spring, the influence of CO &  $SO_2$  on  $O_3$  is opposite to that of  $NO_x$  while in pre-monsoon season, the influence of  $NO_x$  and  $SO_2$  is opposite to that of CO. In post monsoon season, the influence of CO &  $SO_2$  on  $O_3$  is opposite to that of  $NO_x$ . However, the degree of correlation is different in different seasons. Negative

correlation between NO<sub>x</sub> and O<sub>3</sub> concentrations suggested that NO<sub>x</sub> is not the only factor contributed to elevated O<sub>3</sub> concentrations [29].

### 4.2. Influence of NO<sub>x</sub>, CO and SO<sub>2</sub> on Concentration of O<sub>3</sub> in Rohtak

The NO<sub>x</sub>, CO and SO<sub>2</sub> variations and their influences on concentration of O<sub>3</sub> in the ambient air in Rohtak are presented in Figure 5, Figure 6 & Figure 7 and the results of regression analysis are presented in Table 3.

It can be seen that the monthly mean concentration of O<sub>3</sub> was observed to be maximum in the month of September and minimum in the month of July while NO<sub>x</sub>, CO and SO<sub>2</sub> observed to be maximum in the month of July, January and February respectively and minimum in the months of November, October and July respectively.

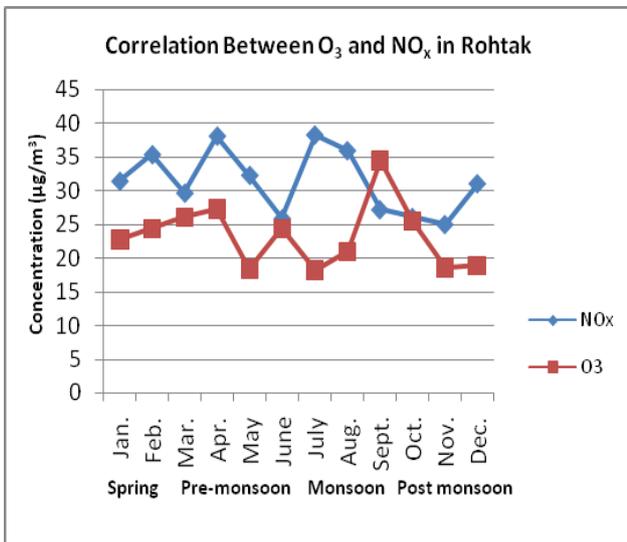


Figure 5. Correlation between NO<sub>x</sub> and O<sub>3</sub> in Rohtak

The maxima of NO<sub>x</sub> and minima of O<sub>3</sub> in month of July is significant and justify the chemistry of O<sub>3</sub> in the atmosphere in comparatively less polluted and less rainfall plain area[30].

Regression analysis results shows that, O<sub>3</sub> is negatively correlated with NO<sub>x</sub> in spring ( $r^2 = -0.797$ ), pre-monsoon ( $r^2 = -0.819$ ) and Post monsoon ( $r^2 = -0.797$ ) seasons and positively correlated during monsoon ( $r^2 = 0.997$ ) season. It may be due to low rainfall in Rohtak in the year 2015. CO showed negative correlation with O<sub>3</sub> during monsoon ( $r^2 = -0.829$ ) season and positive correlation during spring ( $r^2 = 0.991$ ), pre-monsoon ( $r^2 = 0.721$ ) and post monsoon

( $r^2 = 0.997$ ) seasons. SO<sub>2</sub> showed weak negative correlation with O<sub>3</sub> in pre-monsoon ( $r^2 = -0.148$ ) season and positive correlation during spring ( $r^2 = 0.155$ ), monsoon ( $r^2 = 0.843$ ) and post monsoon ( $r^2 = 0.967$ ) seasons. During monsoon season, NO<sub>x</sub> and SO<sub>2</sub> showed positive correlation with O<sub>3</sub> while CO negative correlation. In spring and post monsoon, the influence of CO and SO<sub>2</sub> is opposite to that of NO<sub>x</sub> while in pre-monsoon, the influence of NO<sub>x</sub> and CO on O<sub>3</sub> is opposite to that of SO<sub>2</sub>.

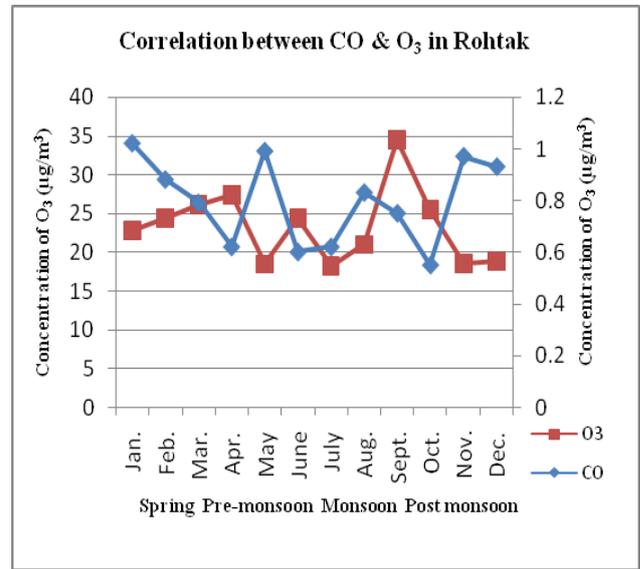


Figure 6. Correlation between CO and O<sub>3</sub> in Rohtak

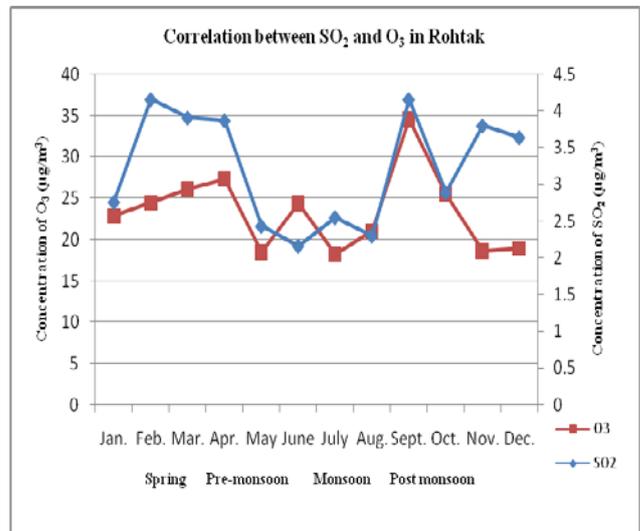


Figure 7. Correlation between SO<sub>2</sub> and O<sub>3</sub> in Rohtak

Table 3. Correlation coefficient and the regression equation between NO<sub>x</sub>, CO, SO<sub>2</sub> and O<sub>3</sub> in Rohtak

Season (Rohtak)	NO <sub>x</sub> Range (Monthly mean) (µg/m <sup>3</sup> )	r <sup>2</sup>	O <sub>3</sub> Equation	CO Range (mg/m <sup>3</sup> )	r <sup>2</sup>	O <sub>3</sub> Equation	SO <sub>2</sub> range (µg/m <sup>3</sup> )	r <sup>2</sup>	O <sub>3</sub> Equation
Spring	29.67-35.34	-0.797	O <sub>3</sub> = -0.179 NO <sub>x</sub> + 30.295	0.79-1.02	0.991	O <sub>3</sub> = -0.013 CO + 0.037	2.76-4.16	0.155	O <sub>3</sub> = 1.6641 SO <sub>2</sub> + 18.4725
Pre-monsoon	25.90-38.07	-0.819	O <sub>3</sub> = 0.224 NO <sub>x</sub> + 16.257	0.60-0.99	0.721	O <sub>3</sub> = -0.019 CO + 0.038	2.16-3.87	-0.148	O <sub>3</sub> = 3.7260 SO <sub>2</sub> + 10.8732
Monsoon	27.23-38.24	0.997	O <sub>3</sub> = -1.501 NO <sub>x</sub> + 75.349	0.62-0.83	-0.829	O <sub>3</sub> = 0.024 CO + 0.007	2.30-4.16	0.843	O <sub>3</sub> = 8.2948 SO <sub>2</sub> - 0.3055
Post monsoon	25.05-31.07	-0.797	O <sub>3</sub> = -0.385 NO <sub>x</sub> + 31.580	0.55-0.97	0.997	O <sub>3</sub> = -0.017 CO + 0.035	2.89-3.80	0.967	O <sub>3</sub> = -7.9436 SO <sub>2</sub> + 48.382

### 4.3. Influence of NO<sub>x</sub>, SO<sub>2</sub> and CO on Concentration of O<sub>3</sub> in Panchkula

The NO<sub>x</sub>, CO and SO<sub>2</sub> variations and their influences on concentration of O<sub>3</sub> in the ambient air in Panchkula are presented in Figure 8, Figure 9 & Figure 10 and the results of regression analysis are presented in Table 4. It can be seen that the monthly mean concentration of O<sub>3</sub> was observed to be maximum in the month of September and minimum in the month of December while NO<sub>x</sub>, CO and SO<sub>2</sub> observed to be maximum in the month of October, April and November respectively and minimum in the months of August, July and July respectively. The averaged O<sub>3</sub> concentrations were lower in plains area compared with the mountainous area may be due to the titration effects of high NO<sub>x</sub> emissions in urban areas and summer O<sub>3</sub> production in the plains and mountainous areas are found to be sensitive to NO<sub>x</sub>.

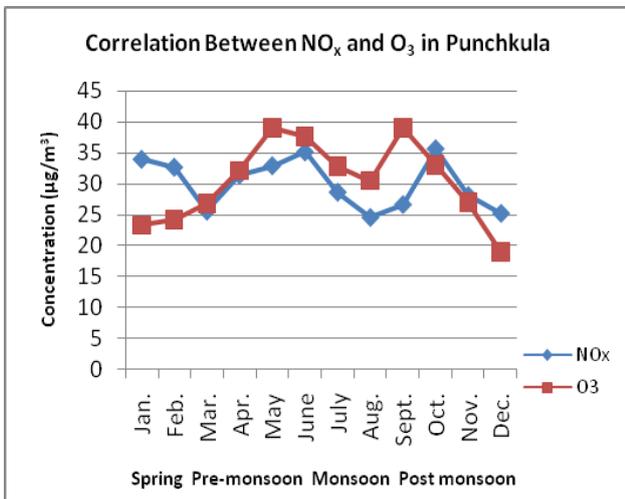


Figure 8. Correlation between NO<sub>x</sub> and O<sub>3</sub> in Panchkula

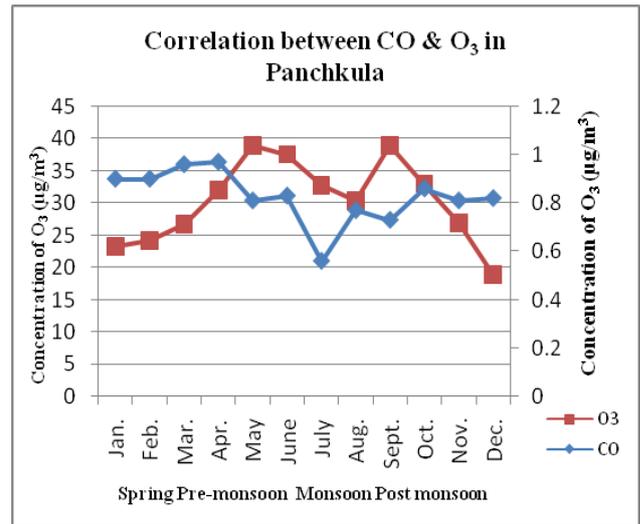


Figure 9. Correlation between CO and O<sub>3</sub> in Panchkula

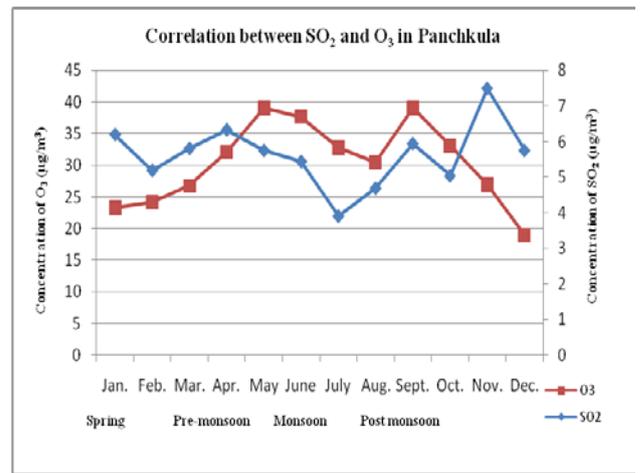


Figure 10. Correlation between SO<sub>2</sub> and O<sub>3</sub> in Panchkula

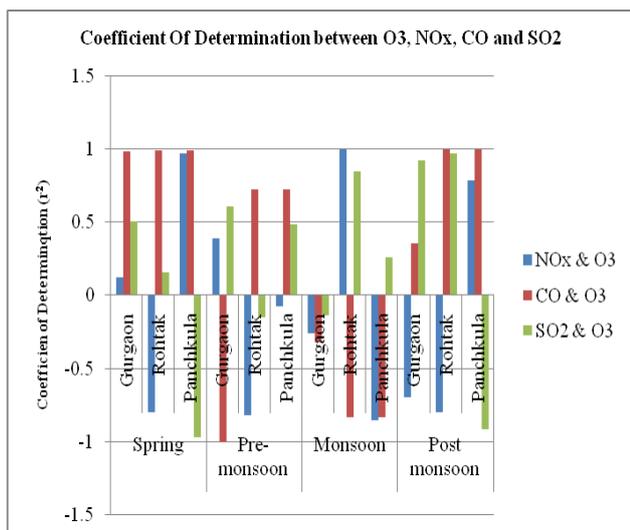
Table 4. Correlation coefficient and the regression equation between NO<sub>x</sub>, CO, SO<sub>2</sub> and O<sub>3</sub> in Panchkula

Season (Panchkula)	NO <sub>x</sub> Range (Monthly mean) (µg/m <sup>3</sup> )	r <sup>2</sup>	O <sub>3</sub> Equation	CO Range (mg/m <sup>3</sup> )	r <sup>2</sup>	O <sub>3</sub> Equation	SO <sub>2</sub> range (µg/m <sup>3</sup> )	r <sup>2</sup>	O <sub>3</sub> Equation
Spring	25.56-33.90	0.971	O <sub>3</sub> = -0.394 NO <sub>x</sub> + 36.879	0.90- 0.96	0.991	O <sub>3</sub> = 0.049 CO - 0.020	5.19-6.20	-0.965	O <sub>3</sub> =-0.4641 SO <sub>2</sub> +27.431
Pre-monsoon	31.38-35.09	-0.074	O <sub>3</sub> = 1.324 NO <sub>x</sub> - 7.605	0.81-0.97	0.721	O <sub>3</sub> = -0.042 CO +0.073	5.44-6.33	0.484	O <sub>3</sub> =-6.9292 SO <sub>2</sub> +76.703
Monsoon	24.55-28.61	-0.854	O <sub>3</sub> = 0.590 NO <sub>x</sub> + 18.382	0.56-0.77	-0.829	O <sub>3</sub> =0.003 CO + 0.032	3.91-5.94	0.262	O <sub>3</sub> =3.4404 SO <sub>2</sub> +17.409
Post monsoon	25.21-35.58	0.784	O <sub>3</sub> = 1.247 NO <sub>x</sub> - 10.606	0.81-0.86	0.997	O <sub>3</sub> = 0.187 CO - 0.129	5.04-7.49	-0.917	O <sub>3</sub> =-1.1443 SO <sub>2</sub> +33.299

Since Panchkula is situated in Hilly area and characterized with comparatively high rainfall, high peak temperature and less population density and so influence of NO<sub>x</sub>, CO and SO<sub>2</sub> on O<sub>3</sub> is observed to be different from Gurgaon and Rohtak. The variation trends of O<sub>3</sub> & NO<sub>x</sub> and O<sub>3</sub> & CO observed to be similar but of O<sub>3</sub> & SO<sub>2</sub> observed to be different in post monsoon season.

Regression analysis shows that O<sub>3</sub> is negatively correlated with NO<sub>x</sub> in pre- monsoon (r<sup>2</sup>= - 0.074) and monsoon (r<sup>2</sup>= -0.854) seasons and positively correlated during spring (r<sup>2</sup>=0.971) and post monsoon (r<sup>2</sup>=0.784) seasons. CO showed negative correlation with O<sub>3</sub> during

monsoon (r<sup>2</sup>= - 0.829) season and positive correlation during spring (r<sup>2</sup>=0.991), pre-monsoon (r<sup>2</sup>=0.721) and post monsoon (r<sup>2</sup>=0.997) seasons. SO<sub>2</sub> showed negative correlation with O<sub>3</sub> in spring (r<sup>2</sup>= - 0.965) and post monsoon (r<sup>2</sup>= - 0.917) seasons and positive correlation during pre-monsoon (r<sup>2</sup>=0.484) and monsoon (r<sup>2</sup>=0.262) seasons. During monsoon season, NO<sub>x</sub> and CO showed negative correlation with O<sub>3</sub>, while SO<sub>2</sub> positive correlation. In spring, pre-monsoon and post monsoon, the influence of NO<sub>x</sub> and CO on O<sub>3</sub> is opposite to that of SO<sub>2</sub>, however the nature of correlation reverses. These results are graphically shown in Figure 11.



**Figure 11.** Correlation Coefficient between O<sub>3</sub>, CO and SO<sub>2</sub> at three measuring sites

From above results, it can be seen that the seasonal effects plays significant role in regulating the concentration of O<sub>3</sub>, NO<sub>x</sub>, CO and SO<sub>2</sub> [31,32,33,34]. Change of season reverses the sign of correlation. The influence of NO<sub>x</sub> and CO concentration on O<sub>3</sub> concentration observed to be similar for spring and post monsoon seasons but not for SO<sub>2</sub>. The effect of rainfall in regulating the concentration of NO<sub>x</sub>, CO and SO<sub>2</sub> and their influence in regulating the concentration of O<sub>3</sub> are of significance.

## 5. Conclusions

The influences of NO<sub>x</sub>, CO and SO<sub>2</sub> concentrations on concentration of O<sub>3</sub> were evaluated for spring, pre-monsoon, monsoon and post monsoon seasons of 2015 in Gurgaon, Rohtak and Panchkula using regression analysis and the findings are stated below.

(i) In Gurgaon, O<sub>3</sub> is negatively correlated with NO<sub>x</sub> in spring ( $r^2 = -0.124$ ), monsoon ( $r^2 = -0.256$ ) and Post monsoon seasons ( $r^2 = -0.694$ ) and positively correlated during pre-monsoon season ( $r^2 = 0.389$ ). CO showed negative correlation with O<sub>3</sub> during pre-monsoon ( $r^2 = -0.999$ ) and monsoon ( $r^2 = -0.322$ ) seasons and positive correlation during spring ( $r^2 = 0.980$ ) and post monsoon ( $r^2 = 0.356$ ) seasons. SO<sub>2</sub> showed weak negative correlation with O<sub>3</sub> in monsoon ( $r^2 = -0.137$ ) season and positive correlation during spring ( $r^2 = 0.506$ ), pre-monsoon ( $r^2 = 0.605$ ) and post monsoon ( $r^2 = 0.922$ ) seasons. During monsoon season, NO<sub>x</sub>, CO and SO<sub>2</sub> showed negative correlation with O<sub>3</sub>.

(ii) In Rohtak, O<sub>3</sub> is negatively correlated with NO<sub>x</sub> in spring ( $r^2 = -0.797$ ), pre-monsoon ( $r^2 = -0.819$ ) and Post monsoon ( $r^2 = -0.797$ ) seasons and positively correlated during monsoon ( $r^2 = 0.997$ ) season. CO showed negative correlation with O<sub>3</sub> during monsoon ( $r^2 = -0.829$ ) season and positive correlation during spring ( $r^2 = 0.991$ ), pre-monsoon ( $r^2 = 0.721$ ) and post monsoon ( $r^2 = 0.997$ ) seasons. SO<sub>2</sub> showed weak negative correlation with O<sub>3</sub> in pre-monsoon ( $r^2 = -0.148$ ) season and positive correlation during spring ( $r^2 = 0.155$ ), monsoon ( $r^2 = 0.843$ ) and post monsoon ( $r^2 = 0.967$ ) seasons. During monsoon season, NO<sub>x</sub> and SO<sub>2</sub> showed positive correlation with O<sub>3</sub> while CO negative correlation.

(iii) In Panchkula, O<sub>3</sub> is negatively correlated with NO<sub>x</sub> in pre-monsoon ( $r^2 = -0.074$ ) and monsoon ( $r^2 = -0.854$ ) seasons and positively correlated during spring ( $r^2 = 0.971$ ) and post monsoon ( $r^2 = 0.784$ ) seasons. CO showed negative correlation with O<sub>3</sub> during monsoon ( $r^2 = -0.829$ ) season and positive correlation during spring ( $r^2 = 0.991$ ), pre-monsoon ( $r^2 = 0.721$ ) and post monsoon ( $r^2 = 0.997$ ) seasons. SO<sub>2</sub> showed negative correlation with O<sub>3</sub> in spring ( $r^2 = -0.965$ ) and post monsoon ( $r^2 = -0.917$ ) seasons and positive correlation during pre-monsoon ( $r^2 = 0.484$ ) and monsoon ( $r^2 = 0.262$ ) seasons. During monsoon season, NO<sub>x</sub> and CO showed negative correlation with O<sub>3</sub>, while SO<sub>2</sub> positive correlation.

(iv) Seasonal effects plays significant role in regulating the concentration of O<sub>3</sub>, NO<sub>x</sub>, CO and SO<sub>2</sub>.

Change of season reverses the sign of correlation. The influence of NO<sub>x</sub> and CO concentration on O<sub>3</sub> concentration observed to be similar for spring and post monsoon seasons but not for SO<sub>2</sub>. The effect of rainfall in regulating the concentration of NO<sub>x</sub>, CO and SO<sub>2</sub> and their influence in regulating the concentration of O<sub>3</sub> are of significance.

The results of this study will be useful for further research on interactions between atmospheric pollutants and Ozone in other region of Haryana and adjoining states in India.

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