

Seasonal Variability of Trace Gases (O_3 , NO , NO_2 and CO) and Particulate Matters (PM_{10} and $PM_{2.5}$) over Delhi

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ABSTRACT

Continuous measurements of particulate matters ($PM_{2.5}$ and PM_{10}) and trace gases (O_3 , NO , NO_2 and CO) have been carried out at 8 different sites over Delhi to evaluate the ambient air quality of city during October 2010 to March 2013. The annual average mixing ratios of ambient O_3 , NO , NO_2 and CO were recorded as 23.8 ± 10.9 ppb, 27.0 ± 18.0 ppb, 16.3 ± 6.8 ppb, and 1.62 ± 0.69 ppm respectively. The seasonal variation of these trace gases (O_3 , NO , NO_2 and CO) are prominent with different amplitudes at these sites of Delhi. The linear correlation of surface O_3 with NO , NO_2 and CO suggests that the precursor gases have influenced the magnitude of O_3 . The annual average concentrations of $PM_{2.5}$ and PM_{10} over Delhi are recorded as 146.0 ± 72.6 $\mu g m^{-3}$ and 245.7 ± 112.1 $\mu g m^{-3}$ respectively, which exceed the values of the national ambient air quality standards.

Keywords: Particulate matters, trace gases, ambient air quality, spatial variability.

1. Introduction

It has been recognized that megacities play significant role in atmospheric chemistry. Several coordinated observations (MEGAPOLI-CORDIS, MIRAGE, MILAGRO, IPAC-NC, REPARTEE etc) have characterized urban air quality, emission of couple of megacities (Mexico, New York, Beijing, Tokyo, Paris etc) and their impact on regional climate. There are approximately ~20 cities having population exceeding 10 million worldwide. According to the United Nations, half of the world's population now lives in cities. In future, the number of megacities and their population density will increase considerably (United Nations, 2007). This will definitely influence the atmospheric oxidizing capacity local and regional levels. Therefore, it has become essential to develop and evaluate integrated methods to improve the megacity emission data, investigate physical and chemical processes.

Delhi is distributed over 1484 km² with population density of 11450/km² and surrounded by highly industrialized National Capital region (NCR) with population density of 1050/km². The sources of atmospheric pollutants are localized and heterogenous and depended on season (Gurjar et

al., 2004, Goyal et al., 2006, Nagpure et al., 2013, Mohan et al., 2012). The combination of factors including industries, power plants, domestic combustion of coal and biomass, and transport (direct vehicle exhaust and indirect road dust) is contributing to air pollution (Garg et al., 2006, Gurjar et al., 2004, 2008). To meet the challenge of urban growth (from 13.9 million to 16.6 million in 2007) in Delhi, several steps (introduction of CNG in public transport, relocation of industries and introduction of Metro transport etc) have been initiated. Even though, the total vehicle population in Delhi has amounted to more than that of three metros, Mumbai, Kolkata and Chennai, put together. In 2021, the projected population will be order of 23.0 million. Assessment of pollution level in Delhi is essential to mitigate the continuous emission within Delhi in addition to the advection of pollutants from NCR region and keep closet to pristine form (State Environment Report for Delhi, 2010).

Earlier most of the study on air quality in Delhi is based on sporadic single station monitoring data, which could not explain the spatial heterogeneity of atmospheric chemistry over Delhi covered with residential, industrial and traffic/commercial zone. These data are mostly collected under individual

research project. These studies (Ali et al, 2004, 2012; Ganguly, 2009; Chelani, 2009; Kumari, 2013; Saxena and Ganguly, 2011; Lal, 2007; Jain et al, 2005; Ghude et al, 2008) show the occasional occurrence of very high surface ozone (~100 ppbv) during summer and some special events e.g., Diwali, irrespective of location over Delhi. In addition, it has also been observed that emission of primary pollutants could not only be responsible for the precursor gases (CO, NO_x, VOCs) for the O₃ production but also for the local atmospheric chemistry. Coordinated observation of precursor gases (CO, NO_x, VOCs) is absent over Delhi except few individual efforts (Singh et al, 2012; Tarsolia et al, 2011; Pandit et al, 2011; Padhy and Varshney, 2000; Srivastava, 2005).

During Commonwealth Games, to forecast and nowcast the air quality index, observation of atmospheric pollutants had been initiated at ten sites of Delhi. Several research articles through development of inventory, observation and modeling (Beig et al, 2013; Marrapu et al, 2014; Sahu et al, 2011, 2012; Gargava et al, 2014; Ali et al, 2013; Chate et al, 2014) reported the air quality of Delhi particularly during Commonwealth Games at these sites. However, the short period result (September-October 2010) depicts the anthropogenic chemical picture of Delhi which confirms earlier observation. Similar efforts were made by research group from China during 2008 Beijing Olympic Games (Wang et al, 2008, 2009a, 2009b, 2010; Street et al, 2010). However, long period data with network of observations are essential as the growing population and human activities increase the atmospheric pollution which is e.g. the cause of the dense fog, smog and haze during winter season (December and January) every year (Singh et al, 2004, 2005) and seasonal changes in demand for fuel and natural pollution result in differing sources during the summer and

the winter months.

In this study, we present the spatial-seasonal variations of surface O₃, NO, NO₂, and CO along with particulate matter (PM₁₀ and PM_{2.5}) over eight different sites of Delhi during October 2010 to March 2013 to evaluate the ambient air quality of the mega city.

2. Methodology

2.1 Description of sites:

Surface O₃, NO, NO₂, and CO were measured simultaneously along with particulate matter (PM₁₀ and PM_{2.5}) at 8 different sites (CV Raman (Site 1), CRRI (Site 2), Delhi University (Site 3), IITM (Site 4), IMD, Aya Nagar (Site 5), IMD, Lodhi Road (Site 6), NCMRWF (Site 7) and IGI Airport (Site 8)) across the Delhi during October 2010 to March 2013 as shown in Fig. 1. The characteristics/details of the sampling sites across the Delhi which generally represents an urban atmosphere, surrounded by huge roadside traffic are summarized in Table 1. Since we consider traffic could be of the major sources of pollutants in mega city like Delhi, it is to be reminded that the total number of registered vehicles in the city was of the order of 7.77 million in 2012-13 (Delhi Statistical Handbook 2012). This area is under the influence of air mass flow from north-east to north-west in winter and from south-east to South-west in the summer. In addition, Delhi experiences severe fog and haze weather conditions and poor visibility during wintertime. The occasional occurrence of dust storm may contribute the presence of mineral dust significantly to the aerosol loading in the summertime. The temperature of Delhi varies from minimum (monthly ave. ~ 13.2°C) in winter (November to February) to maximum (monthly ave. 35.6°C) in summer (March to June). The average rainfall in Delhi during monsoon (July to October) is of the order of ~825 mm.

TABLE 1 DESCRIPTION OF OBSERVATIONAL SITES

Seasonal variations (based on daily averaged value) of PM₁₀, PM_{2.5}, O₃, NO, NO₂, CO and CO₂ at various locations of Delhi, India

Sites	Name of the locations	Latitudes and longitudes	Type
Site 1	CV Raman, Dheerpur, Delhi	28.73°N, 77.20°E	Traffic
Site 2	CRRI, Delhi	28.55°N, 77.28°E	Traffic
Site 3	Delhi University, Delhi	28.69°N, 77.21°E	Traffic and institutional area
Site 4	IITM, New Delhi	28.63°N, 77.18°E	Traffic and agriculture
Site 5	IMD, Aya Nagar, Delhi	28.48°N, 77.13°E	Traffic and agriculture
Site 6	IMD, Lodhi Road, Delhi	28.59°N, 77.24°E	Traffic
Site 7	NCMRWF, Noida	28.63°N, 77.36°E	Traffic and institutional area
Site 8	IGI Airport, Palam, Delhi	28.56°N, 77.09°E	Traffic

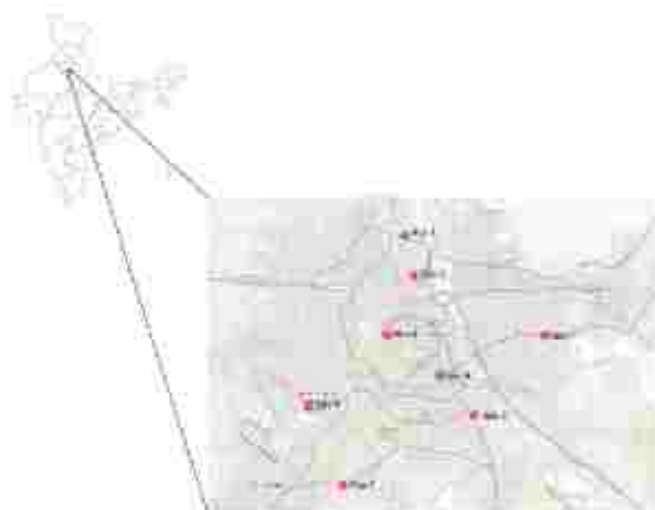


Fig. 1 Map of observational sites over Delhi

2.2 Experimental set up

Mass concentrations of PM₁₀ and PM_{2.5} were continuously measured using beta attenuation particle monitor (BAM) (FH 62 C14; M/s. Thermo Fisher Scientific Inc., USA) which uses the industry proven principle of beta rays attenuation. The measurement principle involves emission, by a small ¹⁴C (Carbon 14) element, of a constant source of high energy electrons known as beta rays through a spot of clean glass fibre filter tape. These beta rays are detected and counted by a sensitive scintillation counter to determine a zero reading. The BAM automatically advances this spot of tape to the sample nozzle, where a vacuum pump then pulls a measured and controlled amount of dust laden air through the filter tape loading it with ambient dust. This dirty spot is placed back between the beta source and the detector thereby causing an attenuation of the beta ray signal which is used to determine the mass of the particulate matter on the filter tape and the volumetric concentration of particulate matter in the ambient air. The lower detection limit (LDL) of the instrument is around 1 $\mu\text{g m}^{-3}$ with a resolution of 0.1 $\mu\text{g m}^{-3}$. The span check of the instrument is automatic and is verified hourly.

The mixing ratios of Surface O₃, NO, NO₂ and CO were measured continuously along with particulate matter (PM_{2.5} and PM₁₀) were measured over Delhi using online analyzers. UV-based Ozone analyzer (Model. 49i; M/s. Thermo Fisher Scientific Inc., USA) was used for measurement of surface O₃ at all the sites. The precision of this analyzer is 1 ppb and it was calibrated periodically against Pure Air Generator (PAG) and traceable certified span gas (multi point

calibration) with the help Multi gas calibrator. NO and NO₂ were measured using trace level NO_x-Analyzer (Model. 42i; M/s. Thermo Fisher Scientific Inc., USA) based on chemiluminescence method with lower detection limit (LDL) = ± 0.050 ppb at all the sites. NO_x Analyzer was calibrated periodically using PAG and certified NO span gas (multiple point calibration) with the help Multi gas calibrator. Carbon monoxide (CO) was measured at all the sites using non-dispersive infrared (NDIR) gas filter correlation CO-analyzer (Model. 48i; M/s. Thermo Fisher Scientific Inc., USA). The instrument was calibrated periodically using PAG and traceable certified CO gas.

In addition, the meteorological parameters (i.e., temperature (accuracy $\pm 1^\circ\text{C}$), relative humidity (RH) (accuracy $\pm 3\%$), wind speed (accuracy $\pm 2\%$) and wind direction (accuracy $\pm 2^\circ$) etc.,) were monitored at all the locations by automatic weather station (AWS). The data from all the measurement sites in around Delhi were stored in online data acquisition system located at centralized hub (IMD Lodhi Road, Site 6).

3. Results and Discussion

3.1 Mixing ratios of Trace gases

The mixing ratios of surface O₃, NO, NO₂ and CO were measured at 8 different sites of Delhi from October 2010 to March 2013. The average spatial variations in mixing ratios of surface O₃, NO, NO₂ and CO with inter-annual average values are summarized in Table 2. Maximum average value of surface O₃ (30.3 ± 9.8 ppb) was observed at Site 8, whereas, lowest (18.8 ± 10.0 ppb) was at Site 3. The overall annual average mixing ratio of surface O₃ was recorded as 23.8 ± 10.9 ppb over Delhi for the study period (Table 2). Sharma et al. (2010) have also reported the mixing ratio of surface O₃ at the order of 23.4 ± 1.2 ppb at the urban site of Delhi during winter 2008. The average mixing ratio of ambient NO was observed of the order of 11.99 ± 4.66 ppb with a maximum value 41.62 ppb over Delhi, whereas the average mixing ratio of NO₂ was recorded as 9.67 ± 3.25 ppb (Sharma et al., 2010). At the same observational site Sharma et al. (2010) also reported the CO mixing ratio of the range of 0.81 - 5.62 ppm with an average of 1.66 ± 1.04 ppm. Delhi being a mega city, higher value of surface of surface O₃ was expected than observed value because of vehicular emission consisting of several O₃ precursor gases (NO, NO₂, CO etc). Combined effect of photochemical production, advection towards downstream, chemical destruction could be reason for such low value of surface O₃ over

Delhi. Details analysis of O₃ precursors (NO, NO₂, CO) will give an idea of photochemical production/chemical destruction.

The highest annual average mixing ratio of NO was recorded as 52.1 ± 35.8 ppb at Site 2 followed

by 38.6 ± 19.8 , 28.8 ± 17.7 , 23.0 ± 17.7 , 21.0 ± 14.8 , 19.4 ± 12.3 , 17.3 ± 14.4 and 16.2 ± 12.3 ppb at Site 1, Site 6, Site 7, Site 8, Site 5, Site 3 and Site 4 respectively. During study, the annual average mixing ratio of ambient NO was recorded

TABLE 2
Averaged annual variations of PM₁₀, PM_{2.5}, O₃, NO, NO₂, CO and CO₂ at various locations of Delhi, India

Year	Locations							
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
PM ₁₀ (µg m ⁻³)								
2011	228.1±88.9	225.1±128.5	222.5±136.1	199.3±111.9	206.5±95.7	286.7±87.1	446.5±94.5	193.3±73.3
2012	299.6±146.3	254.2±150.0	261.2±154.0	226.0±132.8	198.5±105.6	208.5±116.1	282.2±168.8	278.3±114.6
Average	228.9±121.9	239.7±124.4	241.9±125.0	211.3±116.1	203.5±101.4	247.6±97.5	354.4±113.4	236.3±99.8
PM _{2.5} (µg m ⁻³)								
2011	98.3±163.0	127.5±94.7	155.2±103.2	125.8±90.4	244.8±64.8	214.7±70.8	275.6±75.2	99.2±48.8
2012	145.5±102.7	129.8±90.7	111.3±109.9	127.8±85.4	112.0±78.8	92.5±73.5	127.8±82.1	147.5±68.5
Average	121.9±79.6	128.7±75.8	133.3±85.6	128.8±82.6	178.1±55.9	153.6±66.7	201.8±75.2	123.4±69.2
O ₃ (ppb)								
2011	22.0±11.7	22.1±10.6	18.1±12.2	23.3±15.6	32.1±16.8	21.5±12.3	13.6±7.0	31.2±9.9
2012	25.0±16.4	22.5±11.6	21.5±8.8	25.2±11.4	24.0±12.4	22.4±13.5	29.0±12.6	29.3±7.8
Average	23.5±11.3	22.3±10.6	18.8±10.0	24.3±11.4	28.1±13.5	22.0±10.7	21.3±9.6	30.3±9.8
NO (ppb)								
2011	43.3±23.4	60.2±31.3	22.8±11.6	20.0±13.1	18.0±8.8	35.7±15.4	26.9±12.1	26.8±17.0
2012	33.3±20.1	43.9±29.2	15.9±5.5	14.6±13.5	14.4±5.3	21.8±12.2	19.1±16.5	15.1±12.6
Average	38.6±19.8	52.1±35.8	19.4±12.2	17.3±14.4	16.2±12.3	28.8±16.7	23.0±17.7	21.0±14.8
NO ₂ (ppb)								
2011	26.9±10.4	24.0±7.4	12.3±9.3	14.4±10.7	13.1±4.1	24.3±4.2	14.5±4.2	20.4±8.4
2012	19.7±2.2	18.7±10.9	11.9±3.6	9.6±3.0	12.1±2.3	9.9±8.1	10.9±2.3	16.6±4.9
Average	24.3±5.7	21.4±6.7	12.1±6.2	12.0±8.1	12.6±3.3	17.1±7.7	12.7±7.8	18.5±6.5
CO (ppm)								
2011	1.44±0.65	1.61±0.81	1.42±0.88	1.38±0.73	1.95±0.41	1.31±0.41	1.82±0.72	1.47±0.73
2012	2.21±0.81	1.64±0.81	1.14±0.69	1.84±0.81	1.84±0.84	1.86±0.84	1.50±0.73	1.59±0.95
Average	1.83±0.68	1.63±0.67	1.28±0.65	1.51±0.84	1.90±0.67	1.49±0.65	1.66±0.68	1.66±0.78

± Standard deviation

as 30.7 ± 18.0 ppb with large spatial variability over Delhi (Table 2). Recently, Sharma et al. (2014a) have reported average mixing ratio of ambient NO as 19.5 ± 4.9 ppb during winter 2012, whereas 21.7 ± 6.3 ppb during summer 2012 at a site of central Delhi. The minimum annual average mixing ratio of NO₂ was recorded as 12.0 ± 8.1 ppb at Site 4, whereas the maximum annual mixing ratio of NO₂ was observed 24.3 ± 5.7 ppb at Site 1. The annual average mixing ratio of NO₂ was recorded as 21.4 ± 6.7 , 12.1 ± 6.2 , 12.6 ± 3.3 , 17.1 ± 7.7 , 12.7 ± 7.9 and 18.5 ± 6.5 ppb at Site 2, Site 3, Site 5, Site 6, Site 7 and Site 8, respectively (Table 2). The annual average mixing ratio of ambient NO₂ was recorded as 16.3 ± 6.8 ppb over Delhi during the study. More or less similar value of NO₂ was also reported by Sharma et al. (2014b) during winter (17.4 ± 1.4 ppb) and summer (16.8 ± 3.1 ppb) seasons of 2012 over Delhi. Ghude et al. (2006) showed that annual mean O₃ concentration was 26 ppbv with a range of hourly average of 7-67 ppbv in 2001.

The annual average mixing ratio of CO was recorded as 1.62 ± 0.69 ppm with non-significant spatial variability over Delhi. The annual average mixing ratio of CO was recorded at Site 1, Site 2, Site 3, Site 4, Site 5, Site 6, Site 7 and Site 8 were 1.83 ± 0.68 , 1.63 ± 0.67 , 1.28 ± 0.65 , 1.51 ± 0.84 , 1.90 ± 0.67 , 1.49 ± 0.65 , 1.66 ± 0.59 and 1.68 ± 0.78 ppm, respectively (Table 2). Sharma et al. (2010) have reported the average mixing ratio of ambient CO as 1.66 ± 1.04 ppm during winter 2008, whereas 1.6 ± 0.5 ppm during winter 2012 (Sharma et al., 2012) at the same site of Delhi.

3.2 Mass concentrations of PM₁₀ and PM_{2.5}

The annual average mass concentration of PM₁₀ was recorded highest (354.4 ± 113.4 µg m⁻³) at Site 7 whereas lowest at Site 5 (203.5 ± 101.4 µg m⁻³) during 2011 to 2012. The annual average mass concentration of PM₁₀ was recorded as 228.9 ± 121.9 , 239.7 ± 124.4 , 241.9 ± 125.0 , 211.3 ± 116.1 , 247.6 ± 97.5 and

238.3 \pm 96.8 $\mu\text{g m}^{-3}$ at Site 1, Site 2, Site 3, Site 4, Site 6, Site 7 and Site 8 respectively. The annual average mass concentration of PM_{2.5} was recorded higher (201.8 \pm 75.2 $\mu\text{g m}^{-3}$) at Site 7 whereas lower at Site 2 (128.7 \pm 75.8 $\mu\text{g m}^{-3}$). The annual and inter-annual concentrations of PM₁₀ and PM_{2.5} masses are summarized in Table 2. The overall average mass concentrations of PM₁₀ and PM_{2.5} were recorded as 245.7 \pm 112.1 and 146.0 \pm 72.6 $\mu\text{g m}^{-3}$ respectively over Delhi during the study. The annual average concentrations of PM₁₀ and PM_{2.5} masses varying spatially over Delhi during study may be due to source strength of PM and meteorological conditions of the observational sites. Recently, more or less similar observations were also reported by several researchers over Delhi however, the concentrations of PM₁₀ and PM_{2.5} reported by them based on single observational sites (Tiwari et al., 2009; Perrino et al., 2011; Tiwari et al., 2013; Mandal et al., 2014; Sharma et al., 2014a). Sharma et al. (2014a) have reported the average mass concentrations of PM₁₀ and PM_{2.5} as 193.3 \pm 27.1 and 151.1 \pm 26.1 $\mu\text{g m}^{-3}$ respectively over Delhi during winter 2012, whereas Tiwari et al. (2009) have reported annual average concentrations of PM₁₀ and PM_{2.5} as 219 \pm 84 and 97 \pm 56 $\mu\text{g m}^{-3}$ respectively over Delhi. The annual average mass concentration of PM₁₀ were recorded as 280.7 \pm 126.10 $\mu\text{g m}^{-3}$ over an industrial area of Delhi during 2011 (Mandal et al., 2014).

3.3 Diurnal and Seasonal Variation of Trace gases and particulates

Fig. 2 shows the diurnal variation of surface O₃, NO, NO₂ and CO at 8 different sites of Delhi during winter, summer and monsoon seasons. Average daytime mixing ratio of surface O₃ was recorded as 31.6 \pm 16.4 ppb, whereas, average nighttime mixing ratio was recorded as 13.1 \pm 3.0 ppb during winter season. Among the seasons, the highest average daytime (44.3 \pm 18.2 ppb) and average nighttime (19.2 \pm 7.8 ppb) mixing ratio of surface O₃ was recorded during summer (Fig. 2), whereas, the minimum average daytime (31.6 surface O₃ was recorded during winter. During monsoon season the daytime mixing ratio of surface O₃ was recorded as 35.3 \pm 14.5 ppb, whereas, average nighttime mixing ratio was recorded as 15.5 \pm 4.5 ppb over Delhi. In the present study, significant diurnal variation of surface O₃ was observed all the seasons (Fig. 2). The maximum mixing ratio was mostly recorded between 1200 - 1800 h during all the seasons. Higher diurnal

variation in average mixing ratio during daytime may be attributed to a sharp increase in O₃ production during the day. Jain et al. (2005) has also reported very high O₃ mixing ratio during the bright sunny days at Delhi. The daytime increase in O₃ mixing ratio is due to active photochemistry of ozone precursors. Variation in O₃ mixing ratio is also influenced by boundary layer processes, regional emission, long range transport and meteorology. The boundary layer height increases after sunrise, reaching a maximum during noontime and descends after sunset. The seasonal average mixing ratios of surface O₃, NO, NO₂ and CO along with ranges (minimum and maximum) these trace gases over 8 different sites of Delhi are summarized in Table 3. The average mixing ratio surface O₃ was recorded as 20.6 \pm 10.0, 28.6 \pm 11.3 and 28.2 \pm 11.4 ppb during winter, summer and monsoon seasons over Delhi.

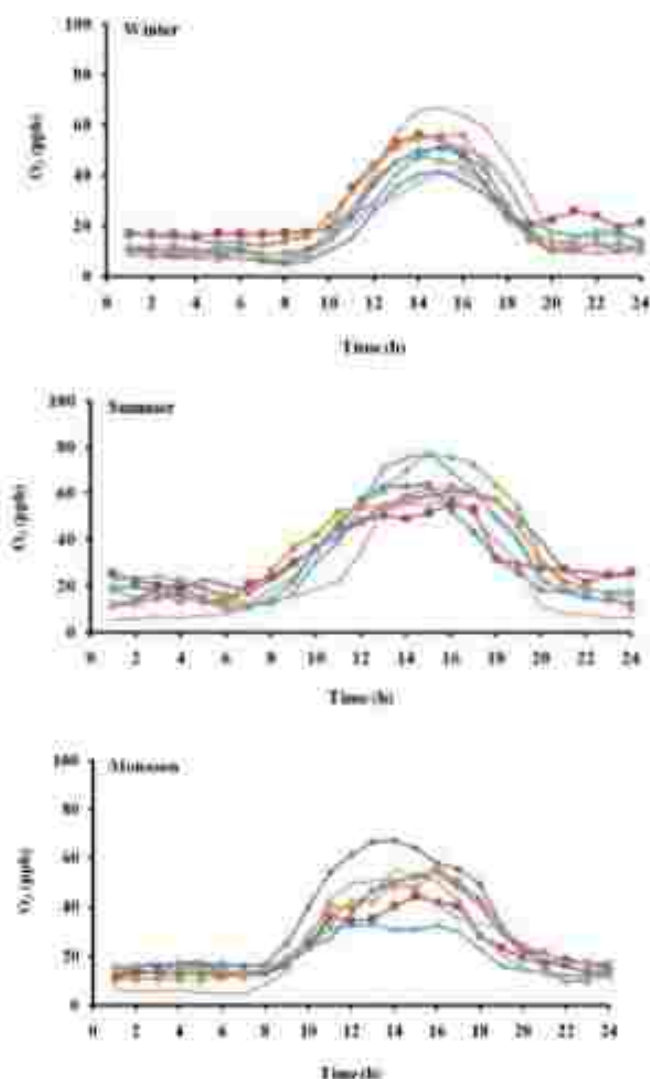


Fig.2 (Ozone)

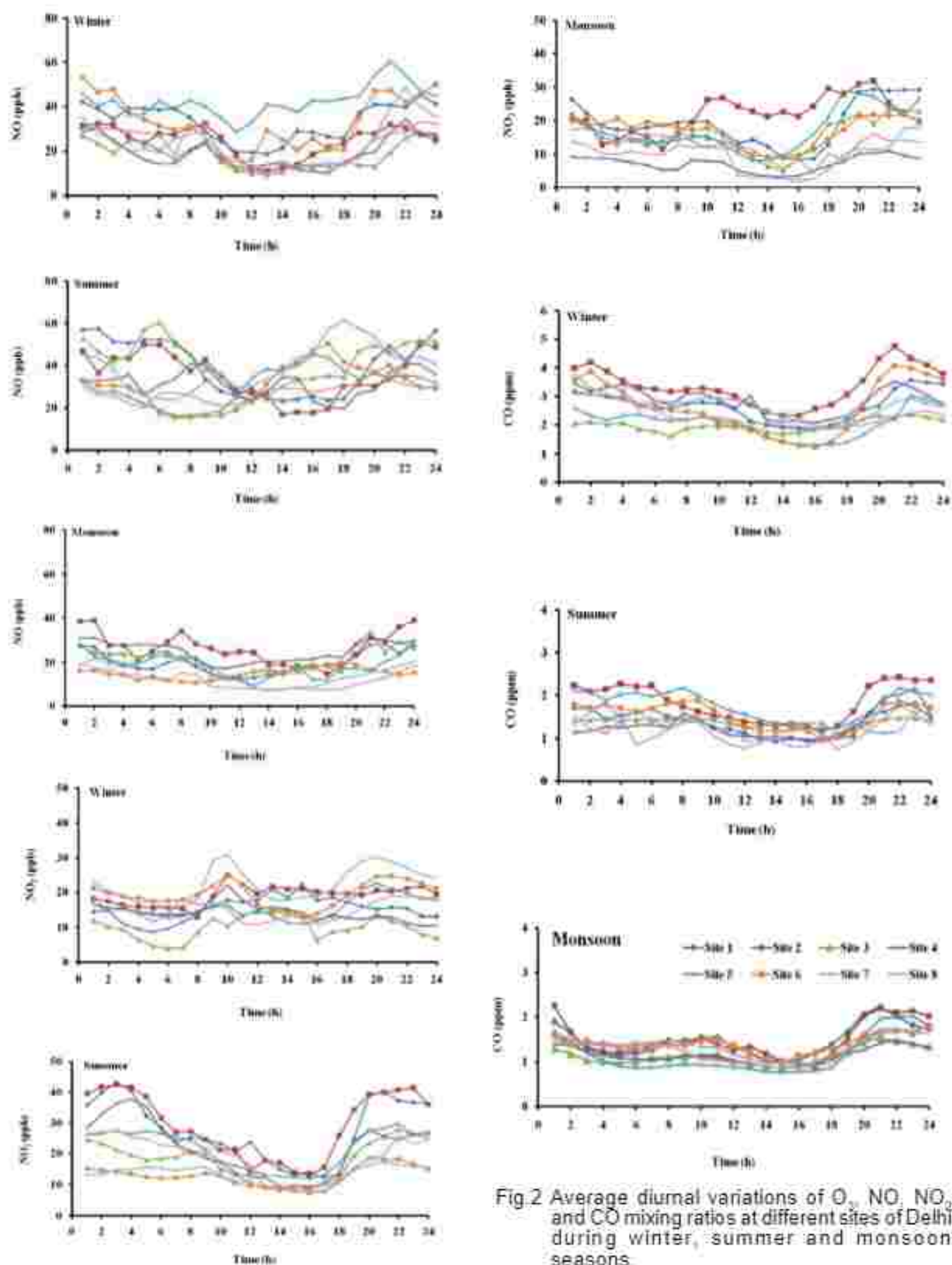


Fig.2 Average diurnal variations of O_3 , NO , NO_2 and CO mixing ratios at different sites of Delhi during winter, summer and monsoon seasons.

TABLE 3

Seasonal variations (based on daily averaged value) of PM₁₀, PM_{2.5}, O₃, NO, NO₂, CO and CO₂ at various locations of Delhi, India

Season	Locations							
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
PM₁₀ (µg m⁻³)								
Winter	351.7±163.0 (54.3-692.9)	310.5±132.1 (51.5-691.3)	321.5±146.4 (50.6-690.1)	281.7±131.0 (36.5-687.4)	234.8±128.8 (39.5-691.9)	278.6±126.7 (37.0-720.0)	352.0±150.4 (38.4-720.8)	235.2±109.8 (31.5-654.0)
Summer	212.1±65.5 (45.3-497.3)	244.2±110.8 (51.5-664.8)	218.5±98.2 (50.6-577.7)	198.3±62.8 (36.5-562.7)	155.0±51.5 (39.5-304.4)	160.5±95.5 (37.2-532.6)	191.4±103.5 (37.4-619.1)	177.8±73.1 (43.5-388.1)
Monsoon	310.3±87.9 (125.8-552.5)	135.4±85.5 (26.8-436.8)	147.8±107.6 (23.0-519.9)	133.1±89.4 (29.9-507.9)	181.8±76.6 (34.2-332.2)	158.3±99.1 (40.1-486.5)	172.4±127.5 (21.2-562.4)	279.9±122.7 (116.4-639.7)
PM_{2.5} (µg m⁻³)								
Winter	199.0±88.8 (32.7-433.7)	178.8±89.0 (28.2-487.7)	203.1±94.3 (36.6-487.5)	183.3±95.2 (26.8-455.4)	151.3±87.9 (32.7-467.3)	154.8±85.8 (32.4-439.1)	206.8±103.3 (34.6-449.4)	144.0±70.8 (35.6-377.3)
Summer	76.3±55.7 (30.3-310.7)	89.3±40.7 (31.1-279.8)	92.3±57.4 (16.7-239.7)	99.4±50.3 (32.9-386.6)	78.7±33.8 (34.9-243.3)	84.8±27.8 (25.9-168.8)	87.7±45.9 (25.5-245.1)	75.1±23.4 (32.2-127.9)
Monsoon	163.9±86.4 (43.2-433.7)	92.7±87.9 (24.6-467.7)	77.3±68.6 (21.4-454.5)	97.7±78.1 (20.6-455.4)	136.8±100.8 (24.9-467.3)	97.2±91.5 (20.9-439.1)	142.0±110.8 (27.6-410.9)	150.3±57.8 (70.6-302.9)
O₃ (ppb)								
Winter	19.8±8.7 (4.3-49.6)	25.4±10.3 (5.3-59.8)	15.7±10.3 (2.6-49.6)	17.6±8.8 (3.3-46.6)	19.6±10.6 (2.1-64.2)	22.6±11.5 (2.9-65.2)	19.2±9.7 (3.6-58.9)	26.0±10.0 (2.4-58.8)
Summer	26.4±12.3 (6.1-59.2)	25.4±12.3 (3.3-63.8)	28.4±9.0 (4.5-44.3)	34.3±13.9 (4.3-72.5)	27.2±9.0 (6.1-44.7)	22.0±11.6 (3.0-48.7)	34.5±11.9 (9.9-65.2)	30.2±10.2 (9.3-58.0)
Monsoon	26.2±12.8 (16.5-71.5)	24.9±12.2 (6.2-48.0)	28.1±8.9 (3.3-54.9)	34.3±14.1 (4.5-50.4)	26.4±9.2 (6.3-56.9)	21.3±11.5 (3.2-66.0)	34.8±12.2 (14.7-55.7)	29.9±10.2 (15.6-57.0)
NO (ppb)								
Winter	45.4±23.7 (12.3-108.3)	61.3±29.0 (3.2-119.7)	26.7±23.0 (2.3-100.9)	18.7±17.3 (2.7-105.8)	14.2±4.3 (7.0-38.7)	31.2±17.7 (3.7-91.4)	17.5±11.9 (3.8-59.4)	21.6±19.4 (3.5-89.2)
Summer	41.4±25.7 (14.2-99.3)	57.0±26.3 (6.3-109.7)	13.7±8.4 (6.0-59.1)	20.4±15.4 (2.3-89.7)	20.2±12.4 (6.9-49.8)	27.5±19.7 (3.6-85.7)	28.1±17.8 (5.3-82.8)	26.0±15.3 (5.7-70.7)
Monsoon	31.9±20.9 (10.3-89.5)	42.5±37.2 (3.4-98.7)	22.2±14.0 (4.6-99.9)	15.1±8.9 (3.1-58.1)	18.8±18.3 (7.0-92.2)	13.0±11.2 (3.8-58.2)	22.6±27.8 (3.3-94.8)	19.2±16.3 (4.2-80.5)
NO₂ (ppb)								
Winter	27.3±15.0 (2.3-55.8)	23.9±9.9 (3.9-55.6)	16.8±10.2 (1.2-45.2)	15.8±9.7 (2.2-45.3)	12.3±2.4 (2.3-21.8)	21.2±8.3 (4.3-54.4)	13.6±6.7 (4.5-43.5)	21.4±11.7 (2.6-58.2)
Summer	27.4±11.5 (9.7-49.4)	27.3±7.3 (9.2-48.1)	10.2±5.1 (4.2-33.3)	16.1±9.1 (3.7-41.4)	11.8±2.5 (9.9-20.2)	11.9±10.9 (2.5-38.2)	14.3±8.6 (5.2-52.4)	18.6±7.8 (2.6-39.6)
Monsoon	26.4±17.1 (5.1-55.1)	15.9±9.7 (2.8-43.3)	13.5±9.6 (2.2-49.0)	8.1±5.5 (1.5-39.5)	16.1±9.6 (9.1-42.5)	7.9±9.8 (1.9-43.0)	13.4±10.4 (4.4-56.1)	23.6±7.4 (11.1-38.8)
CO (ppm)								
Winter	1.91±0.77 (0.42-4.95)	1.57±0.58 (0.13-3.79)	1.82±0.91 (0.15-5.55)	2.24±0.96 (0.32-5.03)	1.90±0.95 (0.38-4.93)	1.88±0.78 (0.27-4.22)	1.83±0.59 (0.70-3.99)	2.17±1.22 (0.15-5.68)
Summer	1.57±0.89 (0.10-3.20)	1.76±0.89 (0.17-4.69)	1.58±0.58 (0.11-4.40)	1.51±0.71 (0.13-3.66)	1.69±0.47 (0.38-3.30)	1.71±0.88 (0.20-3.99)	1.23±0.85 (0.13-3.54)	1.22±0.40 (0.45-2.06)
Monsoon	1.73±0.75 (0.46-3.96)	1.59±0.87 (0.14-3.88)	0.93±0.73 (0.12-3.83)	1.16±0.62 (0.19-4.72)	1.33±0.63 (0.25-2.74)	1.28±0.62 (0.15-2.99)	1.19±0.66 (0.19-2.70)	2.05±0.53 (1.28-3.12)

± Standard deviation; values in parentheses are range

During winter, the daytime mixing ratio of NO was recorded as 21.4 ± 5.7 ppb, whereas, the night time mixing ratio of NO was recorded as 32.7 ± 5.6 ppb (Fig.2). Day time average mixing ratio of ambient NO was recorded as 30.8 ± 9.2 ppb during summer whereas night time mixing ratio of NO was recorded as $38.1 \pm$

6.5 ppb. Day time average mixing ratio (16.4 ± 3.9 ppb) of ambient NO was recorded also recorded significant lower than nighttime mixing ratio (21.9 ± 3.9 ppb) of ambient NO during monsoon season. A significant diurnal variation of ambient mixing ratio of NO was observed throughout the seasons (Fig.2).

During the entire period of study, the mixing ratio of NO was observed high during nighttime and low during daytime. An increase in mixing ratio of ambient in NO_x was also noticed during morning (0700-1000 h) during winter seasons and thereafter decreases to a minimum throughout the daytime (Fig 2), whereas, daytime decrease in NO₂ mixing ratio was also observed during summer and monsoon seasons. Just after sunrise, per-oxy acetyl nitrate (PAN) breaks into NO in sunlight. Because of short lifetime, NO rapidly converts to NO₂ in interaction with O₃ or O₂. However, due to photochemical reaction, NO₂ breaks into NO and O¹D, which produces O₃ in the presence of sunlight. Between morning hours, NO and NO_x (NO_x) mixing ratio started to increase due to the emission of pollutants from the vehicles at most of the sites. During winter season the convective activities and turbulent mixing were weak which leads to lower boundary height. Due to lower boundary layer height, the mixing ratio of pollutants near the surface increases.

The nighttime mixing ratio of ambient CO (2.93 ± 0.37 ppm) was recorded significantly higher than daytime mixing ratio of CO (1.20 ± 0.34 ppm) during winter season (Fig 2). Non-significant day and night time variation in mixing ratio of ambient CO was also observed at Delhi during summer (daytime: 1.28 ± 0.23 ppm; nighttime: 1.62 ± 0.22 ppm) and monsoon (daytime: 1.11 ± 0.15 ppm; nighttime: 1.48 ± 0.26 ppm) seasons (Fig.2). During day time, in presence of UV radiation, CO reacts with water vapor (H₂O) producing OH radical and O¹D in the and leads to formation of surface O₃ in the presence of sufficient NO_x. In the presence of maximum UV radiation, CO and low humidity during day (1200-1400 h) indicates the possibility of photochemical reaction.

Fig.3 shows the diurnal variation in concentrations of PM₁₀ and PM_{2.5} at 8 different sites of Delhi during winter, summer and monsoon seasons. Average daytime concentration of PM₁₀ mass was recorded as 180.3 ± 23.9 µg m⁻³, whereas, average nighttime mixing ratio was recorded as 275.8 ± 44.9 µg m⁻³ during winter season over Delhi. During summer the daytime concentration of PM₁₀ mass was recorded as 216.9 ± 46.1 µg m⁻³, whereas, average nighttime mixing ratio was recorded as 274.2 ± 55.5 µg m⁻³. The

minimum average daytime (130.4 ± 21.7 µg m⁻³) and nighttime (183.1 ± 31.4 µg m⁻³) concentrations of PM₁₀ mass was observed during monsoon season. The nighttime concentration of PM₁₀ mass was recorded significantly higher as compared with daytime of PM₁₀ mass during all the seasons over Delhi. The night time higher concentration of the observational site might be due to lower atmospheric boundary layer and night time temperature (Sharma et al., 2010). The average concentration of PM₁₀ mass was recorded as 297.0 ± 136.0, 198.5 ± 91.1 and 187.4 ± 99.5 µg m⁻³ during winter, summer and monsoon seasons (seasonal average for the period of October 2010 to March 2013) over Delhi. The seasonal average concentrations PM₁₀ and PM_{2.5} alongwith minimum and maximum values (ranges) of 8 different sites over Delhi are summarized in Table-3. Average daytime concentration of PM_{2.5} mass was recorded as 137.8 ± 17.4 µg m⁻³, whereas, average nighttime mixing ratio was recorded as 159.8 ± 25.7 µg m⁻³ during winter season. During summer season, the average daytime concentration of PM_{2.5} mass was recorded as 137.2 ± 17.6 µg m⁻³, whereas, average nighttime mixing ratio was recorded as 164.7 ± 29.3 µg m⁻³. The minimum average daytime (70.6 ± 16.0 µg m⁻³) and nighttime (84.5 ± 13.2

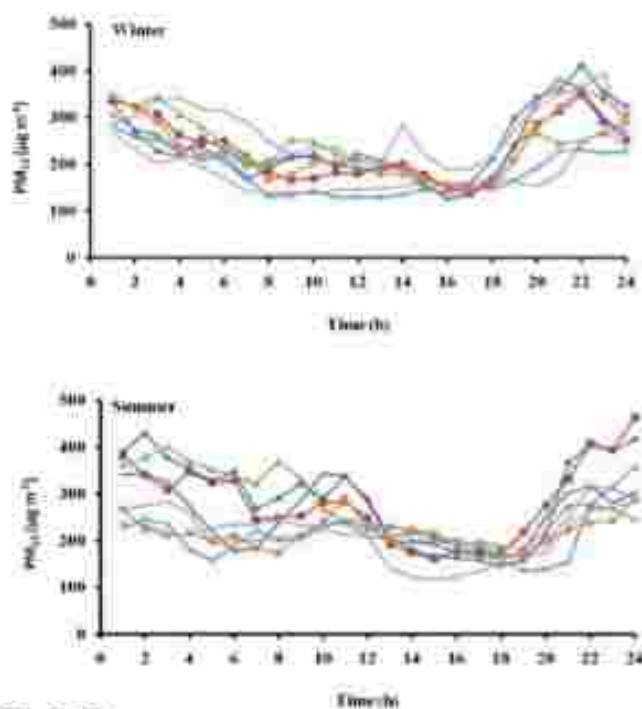


Fig.3 PM₁₀

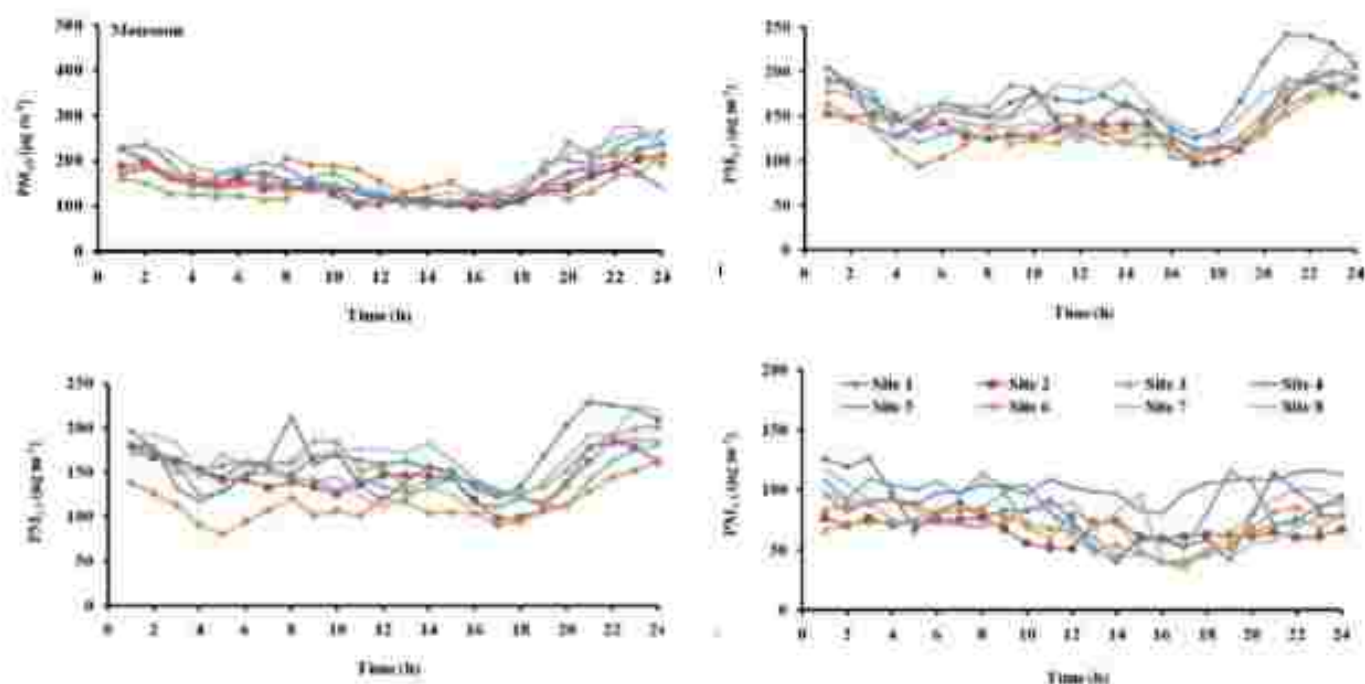


Fig.3 Average diurnal variations in mass concentrations of PM₁₀ and PM_{2.5} at different sites of Delhi during winter, summer and monsoon seasons.

TABLE 4

Seasonal variations (based on daily averaged value) of PM₁₀, PM_{2.5}, O₃, NO, NO₂, CO and CO₂ at various locations of Delhi, India

Season	Locations							
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
PM₁₀ (µg m⁻³)								
Winter	251.7±183.0 (54.3-692.9)	310.5±132.1 (51.5-591.3)	321.5±146.4 (50.6-650.1)	291.7±131.0 (26.5-697.4)	234.8±126.8 (39.5-691.9)	278.6±126.7 (37.0-720.0)	352.0±150.4 (38.4-720.8)	235.2±109.6 (31.5-554.0)
Summer	212.1±65.5 (45.3-497.3)	244.2±110.6 (51.5-564.8)	218.5±95.2 (50.6-577.7)	198.3±82.8 (26.5-582.7)	155.0±81.5 (39.5-604.4)	193.5±95.5 (37.2-582.6)	191.4±103.5 (37.4-619.1)	177.8±73.1 (43.5-389.1)
Monsoon	310.3±97.9 (125.8-552.5)	135.4±85.5 (26.2-436.6)	147.6±107.6 (23.0-519.9)	133.1±89.4 (29.9-507.9)	181.8±76.6 (34.2-322.2)	168.3±99.1 (40.1-486.5)	172.4±127.5 (21.2-562.4)	279.9±122.7 (116.4-639.7)
PM_{2.5} (µg m⁻³)								
Winter	199.0±88.8 (32.7-433.7)	173.6±89.0 (26.2-487.7)	203.1±94.3 (36.6-487.5)	193.3±95.2 (26.8-455.4)	151.3±87.9 (32.7-467.3)	164.6±85.8 (32.4-439.1)	206.6±103.3 (34.6-449.4)	144.0±70.8 (35.6-377.3)
Summer	76.3±35.7 (30.3-210.7)	89.3±40.7 (31.1-279.8)	92.3±57.4 (16.7-239.7)	99.4±50.3 (32.9-336.6)	78.7±33.8 (34.9-243.3)	84.6±27.9 (25.9-166.8)	87.7±45.9 (25.5-245.1)	75.1±23.4 (32.2-127.9)
Monsoon	163.9±96.4 (43.2-433.7)	92.7±87.9 (24.6-487.7)	77.3±68.6 (21.4-454.5)	97.7±78.1 (20.6-455.4)	135.8±100.8 (24.9-467.3)	97.2±91.5 (20.9-439.1)	143.0±110.8 (27.6-410.9)	160.3±57.8 (70.6-302.9)
O₃ (ppb)								
Winter	19.8±8.7 (4.3-49.5)	25.4±10.3 (5.3-59.8)	15.7±10.3 (2.6-49.6)	17.6±8.8 (3.2-46.5)	18.6±10.6 (2.1-64.2)	22.6±11.6 (2.9-65.2)	19.2±9.7 (3.8-58.9)	26.0±10.0 (2.4-58.6)
Summer	26.4±12.3 (6.1-59.2)	25.4±12.3 (3.3-63.9)	26.4±9.0 (4.5-44.3)	34.3±13.9 (4.3-72.5)	27.2±9.0 (6.1-44.7)	22.0±11.6 (3.0-48.7)	34.5±11.9 (9.9-55.2)	30.2±10.2 (9.3-58.0)
Monsoon	26.2±12.6 (16.5-71.5)	24.9±12.2 (6.2-49.0)	28.1±8.9 (3.3-54.9)	34.3±14.1 (4.5-59.4)	26.4±9.2 (6.3-56.8)	21.3±11.5 (3.2-68.0)	34.8±12.2 (14.7-55.7)	29.9±10.2 (15.6-57.0)
NO (ppb)								
Winter	45.4±23.7	61.3±29.0	28.7±23.0	18.7±17.3	14.2±4.3	31.2±17.7	17.5±11.9	21.6±19.4

Locations

Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
	(12.3-108.3)	(3.2-119.7)	(2.3-100.9)	(2.7-105.8)	(7.0-38.7)	(3.7-91.4)	(3.8-58.4)	(3.5-99.2)
Summer	41.4±25.7	57.0 ±26.3	13.7±8.4	20.4±15.4	20.2±12.4	27.5±19.7	28.1±17.8	26.0±15.3
	(14.2-99.3)	(8.3-109.7)	(6.0-59.1)	(2.3-89.7)	(6.9-49.8)	(3.8-95.7)	(5.3-62.8)	(5.7-70.7)
Monsoon	31.9±20.9	42.5 ±37.2	22.2±14.0	15.1±8.9	18.8±18.3	13.0±11.2	22.8±27.8	19.2±16.3
	(10.3-89.5)	(3.4-90.7)	(4.6-99.9)	(3.1-88.1)	(7.0-92.2)	(3.8-58.2)	(3.3-94.8)	(4.2-80.5)
NO ₂ (ppb)								
Winter	27.3±15.0	23.9 ±9.9	16.8±10.2	15.6±9.7	12.3±2.4	21.2±8.3	13.6±8.7	21.4±11.7
	(2.3-55.8)	(3.9-56.6)	(1.2-45.2)	(2.2-45.3)	(2.3-21.6)	(4.3-54.4)	(4.5-43.5)	(2.8-58.2)
Summer	27.4±11.5	27.3 ±7.3	10.2±5.1	16.1±9.1	11.8±2.6	11.9±10.9	14.3±8.6	18.6±7.8
	(9.7-49.4)	(9.2-48.1)	(4.2-33.3)	(3.7-41.4)	(9.9-20.2)	(2.5-38.2)	(5.2-52.4)	(2.6-39.6)
Monsoon	26.4±17.1	15.9 ±9.7	13.6±9.8	9.1±5.5	16.1±9.8	7.9±9.8	13.4±10.4	23.6±7.4
	(5.1-55.1)	(2.9-43.3)	(2.2-49.0)	(1.5-39.5)	(9.1-42.5)	(1.9-43.0)	(4.4-58.1)	(11.1-38.8)
CO (ppm)								
Winter	1.91±0.77	1.57 ±0.58	1.82±0.91	2.24±0.98	1.90±0.98	1.88±0.78	1.83±0.69	2.17±1.22
	(0.42-4.05)	(0.13-3.79)	(0.15-5.55)	(0.32-5.03)	(0.38-4.93)	(0.27-4.22)	(0.70-3.99)	(0.16-5.68)
Summer	1.57±0.89	1.76 ±0.88	1.58±0.58	1.51±0.71	1.99±0.47	1.71±0.88	1.23±0.85	1.22±0.40
	(0.10-3.20)	(0.17-4.68)	(0.11-4.40)	(0.13-3.86)	(0.38-3.30)	(0.20-3.99)	(0.13-3.54)	(0.45-2.06)
Monsoon	1.73±0.75	1.69 ±0.87	0.93±0.73	1.16±0.62	1.33±0.63	1.28±0.62	1.19±0.68	2.05±0.53
	(0.45-3.95)	(0.14-3.88)	(0.12-3.83)	(0.19-4.72)	(0.25-2.74)	(0.15-2.99)	(0.19-2.70)	(1.28-3.12)

± Standard deviation; values in parentheses are range.

$\mu\text{g m}^{-3}$) concentrations of PM_{2.5} mass was observed during monsoon season. The average concentration of PM_{2.5} mass was recorded as 178.3 ± 89.3 , 82.9 ± 39.4 and $93.9 \pm 89.0 \mu\text{g m}^{-3}$. The mass concentrations and their seasonal variability of PM_{2.5} and PM₁₀ were reported by several researchers over Delhi (Tiwari et al., 2009; Tiwari et al., 2010; Sharma et al., 2013; Sharma et al., 2014 a, b) based on the single location. Tiwari et al. (2010) had reported mass concentration of PM_{2.5} of the order of $97.0 \pm 56.0 \mu\text{g m}^{-3}$ whereas, Sharma et al. (2014b) reported mass concentration of PM_{2.5} as $151.2 \pm 26.1 \mu\text{g m}^{-3}$ during winter and as $94.2 \pm 24.6 \mu\text{g m}^{-3}$ during summer season of 2012 over Delhi. The mass concentration of PM₁₀ was observed as $219.0 \pm 84.0 \mu\text{g m}^{-3}$ over Delhi during 2007 (Tiwari et al. 2009) whereas, Sharma et al. (2014b) reported mass concentration of PM_{2.5} as $151.2 \pm 26.1 \mu\text{g m}^{-3}$ during winter and as $94.2 \pm 24.6 \mu\text{g m}^{-3}$ during summer season of 2012 over Delhi.

3.4 Relationship among trace gases

The correlation analysis of average mixing ratio (all observational sites) of O₃ vs NO, O₃ vs NO₂ and O₃ vs CO had been carried out during winter, summer and monsoon seasons over Delhi. In the present study, the mixing ratios of surface O₃ and NO were non-

significant anti-correlated during winter ($r^2 = -0.431$), summer ($r^2 = -0.138$) and monsoon ($r^2 = -0.427$) seasons. Whereas mixing ratios of surface O₃ and NO₂ were non-significant positively correlated during winter ($r^2 = 0.237$), summer ($r^2 = 0.224$) and monsoon ($r^2 = 0.283$) seasons. The seasonal variations of mixing ratios of CO and O₃ were also anti-correlated during winter ($r^2 = -0.597$), summer ($r^2 = -0.477$) and monsoon ($r^2 = -0.460$) seasons.

Photochemical production of O₃ takes place during daytime initiated by oxidation of its precursors. O₃ production during day time is driven by the photochemical reaction between hydroxyl radicals (OH), organic peroxy radicals and NO, while it is removed at night by dry deposition and destruction by alkenes and NO. The conversion of NO to NO₂ by O₃ during the night is the primary reaction that increases NO₂ at night, with the reverse occurring during the day to increase O₃ and decrease NO₂. In addition, the relatively low air temperature near the ground at night could prevent the vertical dispersion of NO_x, contributing to its accumulation and resulting in higher night-time concentrations. Surface O₃ is formed and destroyed by a series of reactions involving NO and NO₂. The O₃ and NO_x mixing ratios show an inverse relationship due to titration of O₃ during daytime. This is similar to observed in

other parts of the world (Chameides and Walker, 1973; Silmans and West, 2009; Sun et al., 2011). According to photochemical reaction, CO reacts with water vapor producing OH radical and O₁D in the presence of UV radiation and leads to formation of ozone in the presence of sufficient NO_x. In the presence of maximum sunlight (UV radiation), low CO and low humidity during midday (1200-1400h) indicates the possibility of photochemical reaction.

4. Conclusions

In the present study, the continuous measurements of surface O₃, NO, NO₂ and CO for the period of October 2010 to March 2013 had been carried along with particulate matter (PM₁₀ and PM_{2.5}) at 8 different sites of Delhi. As expected, maximum surface O₃ was observed during summer followed by monsoon and winter seasons. Significant diurnal variation of surface O₃, NO and NO₂ was observed in all the seasons at most of the observational sites of Delhi. The linear correlation of surface O₃ with NO, NO₂ and CO reveals that the precursor gases have influenced the mixing ratio of surface O₃ at the observational sites of Delhi. The results reveal that the annual average concentrations of particulate matter (PM_{2.5} and PM₁₀) present in the ambient air of Delhi and have close link to surface ozone values.

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