Characteristics of surface ozone in Agra, a sub-urban site in Indo-Gangetic Plain

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In the present study, measurements of surface ozone (O_3) and its precursors (NO and NO_2) were carried out at a sub-urban site of Agra ($27^{\circ}10'N$, $78^{\circ}05'E$), India during May 2012–May 2013. During the study period, average concentrations of O_3 , NO , and NO_2 were 39.6 ± 25.3 , 0.8 ± 0.8 and 9.1 ± 6.6 ppb, respectively. O_3 showed distinct seasonal variation in peak value of diurnal variation: summer > post-monsoon > winter > monsoon. However, NO_2 showed highest levels in winter and lowest in monsoon. The average positive rate of change of O_3 (08:00–11:00 hr) was highest in April (16.3 ppb/hr) and lowest in August (1.1 ppb/hr), while average negative rate of change of O_3 (17:00–19:00 hr) was highest in December (–13.2 ppb/hr) and lowest in July (–1.1 ppb/hr). An attempt was made to identify the VOC– NO_x sensitivity of the site using O_3/HNO_3 ratio as photochemical indicator. Most of the days this ratio was above the threshold value (12–16), which suggests NO_x sensitivity of the site. The episodic event of ozone was characterized through meteorological parameters and precursors concentration. Fine particles ($PM_{2.5}$) cause loss of ozone through heterogeneous reactions on their surface and reduction in solar radiation. In the study, statistical analyses were used to estimate the amount of ozone loss.

Keywords. Surface ozone; O_3/HNO_3 ratio; long-range transport; $PM_{2.5}$.

1. Introduction

Ozone (O_3) is a secondary pollutant which has an important effect on air quality, climate change and atmospheric chemistry (Solomon *et al.* 2000; Sitch *et al.* 2007). Depending on its location in the atmosphere, O_3 can influence human health and climate; in the stratosphere, O_3 filters out detrimental ultraviolet radiations while in the troposphere, it is a constituent of photochemical smog (Gurjar *et al.* 2010). In plants, ozone slows down photosynthetic activity and causes degradation of protein and chlorophyll (Mauzerall and Wang 2001; Fuhrer 2009). Ozone is third most important greenhouse gas (IPCC 2007; Racherla and Adams

2008) and an important source of hydroxyl radicals (OH°).

In the troposphere, O_3 is formed by two major mechanisms: (i) Stratosphere to troposphere transport (Lelieveld and Dentener 2000) and (ii) Photochemical production through the oxidation of carbon monoxide (CO), methane (CH_4), non-methane hydrocarbons (NMHCs) and other volatile organic compounds (VOCs), the reaction is controlled and catalyzed by NO_x (NO and NO_2) (Jonson *et al.* 2006). Biomass burning, fossil fuel combustion, and other anthropogenic activities generate CO, CH_4 , and VOCs (Cetin *et al.* 2003). NO_x is emitted into the atmosphere by natural (microbial activity in soil and lightning, etc.) as well as anthropogenic

sources (biomass burning and combustion of fossil fuel) (Lamarque *et al.* 1996; Bond *et al.* 2001; Beevers *et al.* 2012).

Ozone formation is a highly nonlinear cycle and O_3 has a complex relationship with its precursors (VOCs and NO_x). Depending on ozone's relationship with VOCs and NO_x , two categories of regimes have been classified: NO_x -sensitive and VOC-sensitive (Sillman 1995, 1999). In NO_x -sensitive regime, the rate of ozone production rises with the rise in NO_x concentration while in the VOC-sensitive regime, the rate of ozone production rises with the rise in VOCs concentration. Different models and measurement techniques have been used to identify ozone–VOC– NO_x sensitivity (Peng *et al.* 2006; Kumar *et al.* 2008; Tseng *et al.* 2009). However, three-dimensional photochemical model simulations for evaluation of ozone–VOC– NO_x sensitivity are difficult because of the uncertainties of model assumptions (Fujita *et al.* 1992; Bishoi *et al.* 2009). One alternative approach is to use photochemical indicator species or species ratios such as O_3/NO_y , H_2O_2/HNO_3 , PAN/O_3 , O_3/HNO_3 and NO_x/NO_y (Im *et al.* 2011; Peng *et al.* 2011). Peng *et al.* (2011) conducted their study using photochemical indicators (H_2O_2/HNO_3 , O_3/HNO_3 , O_3/NO_y) at three sites in southern Taiwan and reported two rural sites as NO_x -sensitive and an urban site as VOC-sensitive. In addition to precursors' concentration, ozone levels are significantly influenced by meteorology parameters which play an important role in its formation and transport (Elminir 2005; Tu *et al.* 2007).

Seasonal and diurnal variation of surface ozone and its precursors have been extensively studied at different sites around the world (Aneja *et al.* 1997; Nair *et al.* 2002; Debaje *et al.* 2003; Naja *et al.* 2003; Lehman *et al.* 2004; Satsangi *et al.* 2004; Yang *et al.* 2005; Singla *et al.* 2011; Nishanth *et al.* 2012; Zhang *et al.* 2013). Aneja *et al.* (1997) identified ozone and its relationship with NO , NO_y and CO at downtown, North Carolina. At their site, air-masses were predominantly affected by fresh emissions of CO and NO_y (high NO) which led to low levels of O_3 . Nair *et al.* (2002) carried out their study at the coastal site of Thumba, India and compared it with the urban site of Ahmedabad. At Thumba, despite low levels of CO and NO_x , ozone levels were not significantly low. Naja *et al.* (2003) conducted their study at the high altitude site of Mt. Abu where ozone did not show daytime rise. However, Nishanth *et al.* (2012) observed the daytime increase in ozone levels at

rural coastal site Kannur, India but the seasonal maximum was observed in the winter season. Few studies have also reported variations of ozone and its precursors in Indo-Gangetic Plain (IGP) (Beig and Ali 2006; Lal *et al.* 2008; Shukla *et al.* 2017). Beig and Ali (2006) studied ozone and precursors levels over IGP using model simulations. Lal *et al.* (2008) analyzed trace gases (O_3 , NO_x and CO) during December in Hissar situated in north-western region of IGP. They observed elevated levels of ozone during clear sky days as compared to foggy days and used ratios of different primary emissions to conclude that their site was affected by fresh emissions from biomass burning. Shukla *et al.* (2017) conducted their study at two sites; Varanasi and Lucknow. They compared ground levels measurements of ozone with satellite data which showed significant correlation. Their study also involved correlation analysis of ozone with meteorological parameters.

Earlier studies (Singla *et al.* 2011, 2012) at the present site have focused on diurnal, seasonal variation of ozone, NO and NO_2 . In addition, the effect of different meteorological parameters had also been discussed. However, in recent years, sharp increase in ozone levels is observed which may affect human health as well as staple crops. Therefore, the present study was initiated to add new insights about the relationship of ozone and NO_2 , ozone episodic levels and relationship of ozone and $PM_{2.5}$. The study was designed to determine diurnal and seasonal variations of O_3 and its precursors (NO and NO_2) and their comparison with other geographically different sites in India during May 2012–May 2013. The O_3 –VOC– NO_x sensitivity of the site was determined using O_3/HNO_3 ratio as a photochemical indicator. Further, an O_3 episodic event was analyzed using precursor levels and meteorological parameters. Loss of O_3 through $PM_{2.5}$ was calculated using regression analysis.

2. Site description

The study was carried out at a sub-urban site of Dayalbagh, Agra ($27^{\circ}10'N$, $78^{\circ}05'E$). The site is located in Indo-Gangetic Plain and has a semi-arid climate as it is surrounded by the Thar Desert of Rajasthan on two-thirds of its periphery (figure 1). The detailed description of the site has been discussed elsewhere (Verma *et al.* 2015). The site has four distinct seasons; summer (March–June), monsoon (July–September), post-monsoon

Figure 1. Map of sampling site (shown by star) at Dayalbagh, Agra, India.

(October and November) and winter (December–February). In the summer season, the temperature ranged between 22 and 47°C (avg. $31 \pm 6.8^\circ\text{C}$), while relative humidity (RH) ranged between 14 and 60% (avg. $43 \pm 20\%$). In the winter season, the temperature dropped to below 3°C (avg. $15.5 \pm 6.0^\circ\text{C}$) and relative humidity ranged from 23 to 90% (avg. $70 \pm 20\%$). In the post-monsoon season, temperature ranged from 11 to 38.5°C ($25.9 \pm 6.1^\circ\text{C}$) and RH ranged from 20 to 94% ($64.3 \pm 19\%$). In monsoon season, because of heavy rainfall, RH ranged from 45 to 98% ($78.9 \pm 14.4\%$) and temperature varied from 22 to 40°C ($30.2 \pm 3.1^\circ\text{C}$).

3. Methodology

Continuously operating O_3 (Thermo Fischer Model 49i) and NO_x analyzer (Thermo Fischer Model 42i) have been used for the measurements of surface O_3 and NO_x concentrations, respectively. For sampling, air is passed through a sampling manifold to remove moisture and then through a polytetrafluoroethylene (PTFE) filter ($5\mu\text{m}$, Sartorius AG, Germany) to remove dust and particles before entering the analyzer. The ozone concentration measurement is based on ultraviolet light absorption at 254 nm wavelength. The concentration of ozone in air is calculated by the analyzer using Lambert–Beer law. The detection limit of ozone analyzer is 1.0 ppb, response time is 20 s and accuracy is $\pm 5\%$. The zero drift of ozone analyzer is

<1.0 ppb for 24 hrs. The NO_x analyzer operates on the principle of chemiluminescence. Nitric oxide (NO) present in sample air react with O_3 (generated by the analyzer) to form NO_2 molecules which emit a characteristic luminescence in infrared (IR) region. The intensity of IR radiation is linearly proportional to the NO concentration. Since this method is specific for NO measurements, therefore, NO_2 measurement was based on the conversion of NO_2 into NO using a molybdenum (Mo) converter. Molybdenum has $\sim 100\%$ conversion efficiency (Pitts and Pitts 2000). The detection limit and response time of NO_x analyzer are 0.4 ppb and 80 s, respectively for 60 s averaging time. The zero drift of NO_x analyzer is <0.4 ppb for 24 hrs.

To maintain the accuracy, the analyzers were regularly checked for zero and span calibrations. Zero check was performed on a weekly basis, while span checks were performed on monthly basis. For zero air generation, compressed air is first passed through silica gel then through purafil and charcoal. For span check, ozone analyzer has in-built ozone generator, while for NO_x analyzer, span gas cylinder of NO (NIST traceable NO in N_2) was used through multipoint calibrator (Teledyne model, T700). The data can be recorded at the intervals of 1 min to 24 hr with the help of data acquisition systems. In the present study, 1-hr average data was selected.

Gaseous HNO_3 samples ($N = 60$) were collected to determine NO_x –VOC sensitivity. HNO_3 samples were collected using a low-volume sampler

(vayubodhan) at a flow rate of 2 L min^{-1} . For the collection of HNO_3 , distilled water (25 ml) was used as absorbing media. The collected HNO_3 samples were analyzed by ion chromatography (Dionex ICS-1100) (Kumar *et al.* 2004). The eluent used for analysis was 6.0 mM NaOH and ICS was equipped with a guard column (AG 11) and analytical column (AS11). For standardisation of the method, sodium nitrate ($>99.0\%$ purity) was procured from Sigma-Aldrich (St. Louis, MO, USA). The stock solution of 1000 mg L^{-1} was prepared and stored at -18°C from which working standards were prepared when required. The limit of detection, relative error and relative standard deviation were 5.9 ng m^{-3} , 1.4 and 0.7%, respectively.

$\text{PM}_{2.5}$ samples ($N = 55$) were collected on 47 mm quartz fibre filters (Pallflex, Tissuquartz) using fine particulate sampler (Envirotech APM 550). The detailed description of particulate sample collection and analysis has been discussed elsewhere (Verma *et al.* 2016). The present site being 1300 km inland of sea and has an average RH of $51.2 \pm 14.2\%$, therefore, no correction for RH was made, as it has more significance on coastal aerosols which are hygroscopic in nature. According to Moorthy *et al.* (2010), the effect of RH becomes more significant at $\text{RH} > 80\%$. During the study period, only on 18% of days, RH was greater than 80%. However, to counter this positive artefact, particulate samples were placed in desiccators before and after sampling until their mass was stabilized. Earlier studies have also used the similar method to calculate mass concentration of particulate samples (Clements *et al.* 2014; Yadav *et al.* 2015).

Meteorological parameters, viz., solar radiation, temperature, relative humidity and wind speed were recorded at sampling site using Automatic Weather Station WM271 Data Logger at every 1-hr interval. The monthly mean Planetary Boundary Layer (PBL) height in a grid of $0.5 \times 0.5^\circ$ was calculated from GDAS NOAA ARL (<https://www.ready.noaa.gov/>) daily values. The diurnal variation of temperature, RH and solar radiations (SR) in different seasons over the study period is shown in figure 2(a–c). Diurnal pattern of temperature for four seasons was characterized by high value during daytime ($22\text{--}38^\circ\text{C}$) and low value during the night and early morning ($10\text{--}25^\circ\text{C}$) hours. Solar radiation also showed the similar diurnal pattern in all seasons while relative humidity showed an opposite pattern. The monthly mean PBL height shows highest value (1666 m) in June and lowest (222 m) in December (figure 2d).

4. Results and discussion

4.1 Diurnal variation of ozone and its precursors

At the present site, average concentrations of O_3 , NO, and NO_2 were 39.6 ± 25.3 , 0.8 ± 0.8 and 9.1 ± 6.6 ppb, respectively. Figure 3 shows diurnal pattern of ozone, NO, and NO_2 ; average diurnal pattern of ozone was characterized by minimum value of 20.3 ± 9.6 ppb during early morning hours ($\sim 7:00$ hr), reached a maximum value of 67.2 ± 27.9 ppb during afternoon ($\sim 14:00$ hr), remained more or less steady until $\sim 17:00$ hr, and then decreased until next morning. The diurnal pattern of NO and NO_2 was characterized by two peaks; morning and evening peak. The morning peak of NO (1.5 ppb) was observed at around 7:00 hr and that of NO_2 (11.0 ppb) appeared 1 hr after NO peak. The evening peaks of NO (1.0 ppb) and NO_2 (12.3 ppb) were observed around 22:00 hr. High levels of primary precursors (NO and NO_2) during late evening hours are a combination of anthropogenic emissions, boundary layer processes, chemical reactions and local surface wind pattern. During night hours the boundary layer descends and pollutants released from anthropogenic sources get trapped in shallow boundary layer results in peak concentration around 21:00–23:00 hr. Both NO and NO_2 showed low concentrations during the daytime. Similar variation in diurnal pattern was also reported by earlier studies in India, at urban sites of Ahmedabad (Lal *et al.* 2000) and Hyderabad (Swamy *et al.* 2012); at the rural site of Anantapur (Reddy *et al.* 2012); and at the semi-urban site of Dibrugarh (Bhuyan *et al.* 2014).

4.2 Seasonal variation of O_3 and NO_2

Figure 4 shows a well-defined seasonal variation of O_3 and NO_2 on the diurnal scale. In all the seasons, the diurnal variation pattern of ozone followed almost the same pattern; however, the amplitudes of variation were different; with the highest amplitude in the summer (79.7 ± 15.9 ppb), followed by post-monsoon (73.0 ± 9.5 ppb), winter (58.9 ± 20.5 ppb) and lowest in monsoon (32.0 ± 5.1 ppb) season. High level in summer season was attributed to high temperature; low relative humidity and intense solar radiation which favour photochemical generation of O_3 (figure 2a–c). PBL height was also high in the summer season, which allows the O_3 rich upper tropospheric air to percolate

Figure 2. Diurnal variation of (a) temperature, (b) relative humidity, (c) solar radiation in summer, monsoon, post-monsoon and winter and (d) monthly variation of planetary boundary layer height.

Figure 3. Average diurnal variation of NO, NO₂ and surface O₃ at the study site.

downward and enhance the O₃ concentration near the surface. A similar observation was reported by Bhuyan *et al.* (2014) at a semi-urban site, Dibrugarh and Putero *et al.* (2014) at the global WMO/GAW station Nepal Climate Observatory-Pyramid (NCO-P, 5079 m a.s.l.) in the southern Himalayas. Stratospheric intrusions may result in the rise in upper tropospheric ozone (Sandhya *et al.* 2015). During the monsoon season, washout of precursors may lead to lowest concentration of O₃. Low levels of ozone and NO_x in monsoon season may be attributed to high humidity (O₃ vs. RH, $r = -0.63$; $p < 0.001$) and wet scavenging of ozone and its precursors due to heavy rainfall. At the study site, 97% rainfall was observed in monsoon season; in addition, continuous rainfall for two to

Figure 4. Diurnal variations of O_3 and NO_2 in different seasons.

three days was also observed which lead to trace gas levels below the detection limit. High water content in air may lead to the removal of nitrogen oxides from air to form nitric and nitrous acid because of their high water solubility (Seinfeld and Pandis 2006). Earlier studies have also reported a decrease in O_3 , NO , NO_2 and NO_x levels due to rainfall (Reddy *et al.* 2012; Bhuyan *et al.* 2014; Sharma *et al.* 2016). In addition, during monsoon season the wind direction was predominantly from Arabian Sea in south-west direction; therefore, these air-masses were comparatively clean in nature. However, in other seasons, the dominant wind direction was north, northwest when air-masses passed through industrial and urban locations. At the rural site of Gadanki (Renuka *et al.* 2014) although NO_x levels were very low throughout the year yet ozone levels were reasonably distinct which may be attributed to high levels of VOCs (isoprene and monoterpenes). However, as the present site is NO_x -sensitive, therefore, even the slight decrease

in NO_x may result in the decrease in ozone levels. The diurnal cycle of O_3 and solar radiations followed the same pattern (figures 2c and 4). Solar radiations peak at around 12:00 hr in all the seasons [summer (865 W m^{-2}), monsoon (679 W m^{-2}) and post-monsoon (762 W m^{-2})] except in winter (556 W m^{-2}) season. However, peak O_3 concentration was observed around 13:00–16:00 hr.

NO_2 attained the highest levels during winter ($18.2 \pm 10.3 \text{ ppb}$) season followed by post-monsoon ($14.6 \pm 3.4 \text{ ppb}$), summer ($10.9 \pm 7.9 \text{ ppb}$) and lowest in monsoon ($4.5 \pm 4.4 \text{ ppb}$) season. During winter, NO_2 released from primary sources gets trapped near the surface due to low PBL height resulting in high levels of NO_2 . Low levels in summer months may be due to: (i) dilution of pollutants due to high PBL and (ii) greater photochemical loss due to intense solar radiation.

An analysis of diurnal and seasonal variation of ozone levels at different sites in India was done to elucidate the effect of meteorological parameters

Table 1. Comparison of monthly average maximum and minimum surface ozone (ppb) with other sites in India.

Site		Monthly average minimum and maximum (ppb)	References
Trivandrum	Coastal	11.5 ± 4.7 to 28.1 ± 16.2	David and Nair (2011)
Pantnagar	Sub-urban	10.8 ± 12.1 to 39.3 ± 18.9	Ojha <i>et al.</i> (2012)
Nainital	High-altitude	22.8 ± 7.4 to 62.0 ± 12.0	Sarangi <i>et al.</i> (2014)
Anantapur	Rural	16.5 to 55.7	Gopal <i>et al.</i> (2014)
Gadanki	Rural	9.0 to 37.0	Renuka <i>et al.</i> (2014)
Ahmedabad	Urban	18.1 to 35	Mallik <i>et al.</i> (2015)
Udaipur	Urban	17.4 to 32.0	Yadav <i>et al.</i> (2016)
Delhi	Urban	16.8 ± 6.0 to 40.3 ± 8.7	Sharma <i>et al.</i> (2016)
Varanasi	Urban	22.0 ± 6.9 to 63.9 ± 13.7	Shukla <i>et al.</i> (2017)*
Lucknow	Urban	$14.9 \pm 1.3^{\#}$ to $52.4 \pm 53.5^{\#}$	Shukla <i>et al.</i> (2017)*
Agra	Sub-urban	14.0 ± 9.2 to 57.6 ± 25.5	Present study

*Averages in μgm^{-3} .[#]Minimum is average for Nov.–Dec.; maximum is average for Jan.–Feb.

and precursors (table 1). At the present site, diurnal variation of ozone was characterized high levels during noon and afternoon hours, and seasonal maxima was observed in summer season while minima in monsoon. However, at other sites in India, ozone followed different diurnal and seasonal variations. At the high altitude site in Nainital (Sarangi *et al.* 2014), highest monthly mean (62 ± 12 ppb) was observed in spring season, while lowest in the summer-monsoon season. Diurnal variation is not seen at this high altitude site as ozone levels are influenced by wind flow and PBL height rather than photochemistry. At the rural site Gadanki, the diurnal trend of ozone was almost same as the present site, but ozone and NO_x levels were lower than present site because Gadanki is not affected by vehicular emissions. At the coastal site of Trivandrum, the broad daytime peak of ozone may be attributed to the strong influence of sea and land breeze. At the urban site of Delhi, although monthly average ozone was lower, NO_x levels were very high as compared to the present site (Sharma *et al.* 2016). Similar variation was observed at the urban sites of Lucknow and Varanasi where monthly average O_3 concentrations were lower than the present site, however, at Lucknow NO_x levels were comparatively high and at Varanasi, they were comparable to the present site (Shukla *et al.* 2017). Earlier studies have also reported low levels of NO , NO_2 and NO_x , and high levels of ozone at sub-urban sites as compared to urban sites (Kulkarni *et al.* 2016) as the high levels of NO_x are released from vehicular sources (containing high levels of NO) leading the destruction of ozone. The monthly average minimum and

Table 2. Rate of change of ozone in different months.

Month	Positive rate of change at 08:00–11:00 hr (ppb/hr)	Negative rate of change at 17:00–19:00 hr (ppb/hr)
Jan	2.9	− 9.1
Feb	1.7	− 6.6
Mar	13.8	− 7.2
Apr	16.3	− 7.7
May	15.5	− 7.7
Jun	6.3	− 3.6
Jul	4.0	− 1.1
Aug	1.1	− 1.4
Sep	8.2	− 7.8
Oct	9.1	− 8.3
Nov	10.8	− 11.6
Dec	6.1	− 13.2

maximum of O_3 at the present site were higher than the levels at a sub-urban site of Pantnagar (Ojha *et al.* 2012) and comparable to the levels at a rural site of Anantapur (Gopal *et al.* 2014).

4.3 Rate of change of Ozone

The rate of change of O_3 defines the formation or destruction of O_3 in unit time. Table 2 shows the monthly variation of the rate of change of ozone [$d(\text{O}_3)/dt$] in the morning (08:00–11:00 hr IST) and in the evening hours (17:00–19:00 hr IST). The slope of the regression line corresponds to the rate of change of O_3 concentration. The positive rate of change corresponds

Table 3. Comparison of Rate of change of O_3 with other sites in India.

Site	Rate of change at 08:00–11:00 hr (ppb/hr)	Rate of change at 17:00–19:00hr (ppb/hr)	References
Dayalbagh, Agra (sub-urban site)	7.9	– 6.9	Present study
Mohal (sub-urban valley site)	7.3	– 5.9	Sharma <i>et al.</i> (2013)
Anantapur (rural site)	4.1	– 3.0	Reddy <i>et al.</i> (2008)
Delhi (urban site)	4.5	– 5.3	Ahammed <i>et al.</i> (2006)
Ahmedabad (urban site)	5.9	– 6.4	Lal <i>et al.</i> (2000)

to the O_3 formation, while the negative rate of change corresponds to O_3 loss rate. The average positive rate of change of O_3 was maximum in April (16.3 ppb/hr) and minimum in August (1.1 ppb/hr). Maximum production rate in April may be due to meteorological conditions which favour photochemical generation of O_3 , while the minimum value in August may be due to greater cloud cover resulting in lower photochemical activity and scavenging of its precursors (NO_2 and NO) through rainfall. The average negative rate of change of O_3 was maximum in December (–13.2 ppb/hr) while minimum in July (–1.1 ppb/hr). In table 2, sharp increase in the rate of ozone formation was observed from February to March, however, the rate of destruction was gradual. Ozone formation is a complex process which gets influenced by number of factors, the drastic change in ozone formation rate may be attributed to (i) sharp increase in average temperature during 08:00 – 11:00 hr from February (14.4°C) to March (24.5°C), however, during 17:00–19:00 hr, no distinct variation was observed (February, 23.6°C; March, 25.7°C), (ii) although, there was no significant difference in solar intensity, the duration of solar radiation was increased by 5 hrs in March, (iii) wind speed was high in February as compared to March, (iv) humidity was also high in February (RH = 73%) as compared to March (RH = 50%), (v) difference in morning and evening hours PBL height was also high in March, (vi) in addition, February month had 8–9 cloudy days and rainfall was also observed. Wind direction was same in both the months (west, northwest). A sharp change in the rate of ozone formation and destruction was also observed from August to September. Although there was no significant change in average temperature during 08:00–11:00

hr and 17:00–19:00 hr from August to September, change in relative humidity was significant during 08:00–11:00 hr (in August RH = 80% and in September RH = 68%) and 17:00–19:00 hr (in August RH = 74% and in September RH = 60%). In addition, in August, frequent rainfall may result in low levels of ozone and its precursors due to wet scavenging. On the days of rainfall, the levels of ozone, NO and NO_2 were very low and sometimes below the detection limit. In August, 16–17 days rainfall was observed, in contrast to September when rain occurred only on 2–3 days.

Table 3 shows a comparison of the rate of change of O_3 at the present site with different sites in India. The average rate of change of O_3 (–6.9 ppb/hr) during evening hours was lower than their respective production rate (7.9 ppb/hr) during morning hours. Similar observations were also reported at rural and other sub-urban sites of India (Reddy *et al.* 2008; Sharma *et al.* 2013). At urban sites, Ahmedabad and Delhi, the average negative rate of change during evening hours was higher as compared to the average positive rate of change during morning hours (Lal *et al.* 2000; Ahammed *et al.* 2006). According to Naja and Lal (2002), the higher loss rate at urban sites was attributed to the higher production rate of NO_x from vehicular emissions and fast titration of O_3 in the evening hours.

4.4 Ozone–VOC– NO_x sensitivity

Several photochemical indicators (H_2O_2/HNO_3 , O_3/HNO_3 , O_3/NO_y) have been used in earlier studies to assess O_3 – NO_x –VOC sensitivity (Sillman *et al.* 1997; Peng *et al.* 2011). In the present study, the O_3/HNO_3 ratio was used as an

Figure 5. Seasonal variation of O_3/HNO_3 ratio.

indicator to assess O_3 – NO_x –VOC sensitivity. Sillman (1995) reported that the formation of ozone is VOC-sensitive when the O_3/HNO_3 is below the threshold value (12–16) and this value is true for a moderately polluted environment (Sillman *et al.* 1998; Sillman and He 2002).

During the study period, HNO_3 concentration ranged from 0.3 to 7.0 ppb with average concentration 2.3 ± 1.8 ppb while O_3/HNO_3 ratio ranged from 6.0 to 118.2. Figure 5 shows that the O_3/HNO_3 ratio was above the threshold value in summer, post-monsoon and winter indicating the present site is NO_x -sensitive for most of the time in summer (73%), post-monsoon (70%) and winter (50%). The wet removal of O_3 and HNO_3 through rainfall in monsoon may be responsible for decrease in O_3/HNO_3 ratio; however, the site is predominantly NO_x sensitive.

4.5 Ozone episode analysis

High temperature and intense solar radiation favour photochemical generation of ozone (Tu *et al.* 2007; Shan *et al.* 2009). At the present site, the summer season is associated with high temperature (avg. 31°C), long sunshine duration (8–9 hr) and low relative humidity (avg. 43%). These conditions may lead to days with high O_3 levels, which may be considered as ozone episodes. The most common criteria to identify high ozone episodes are when ozone exceeds air quality standard of environmental agencies at a particular site. Therefore, high ozone episodes were identified when hourly ozone concentration exceeded 90 ppb (NAAQS for India, CPCB 2009). These episodes may be influenced by local photochemistry as well as transport.

One such episodic event was observed, from 6th to 10th May (figure 6). On 5th May, although episodic levels of ozone were not observed, but high levels were observed during night time (45–60 ppb). On 6th May, highest levels (102.8 ppb) of ozone were observed at 14:00 hr when wind speed was low (below 2 m/s). Further on 6th May, high levels of ozone were also observed during late night hours (above 50 ppb) when NO_x levels and wind speed were also high (4–5 m/s). The high levels of ozone during the daytime may be due to local photochemistry and transport; however, night time high levels may be solely due to transport. On 7th May, peak ozone levels were observed at 13:00 hr (106.5 ppb) and high levels of ozone were observed till 21:00 hr (67 ppb). During this episode, wind speed was high (4–5 m/s). On 8th May, peak ozone levels were observed at 12:00 hr (124 ppb), night time levels were low and NO_x levels were slightly higher than consecutive days. Wind speed was moderate during peak ozone hours (2–3 m/s). Similar variation was observed on 9th and 10th May with peak ozone values of 118.2 and 112 ppb, respectively. During all episodic days, the temperature was high and maximum temperature ranged from 43 to 45°C . Relative humidity was low and duration of solar radiation was 7–8 hrs. 11th May was a normal day when peak ozone levels decreased to 78 ppb with a simultaneous decrease in NO_x levels. On this day, a decrease in maximum temperature and an increase in RH and wind speed (3.5–6.5 m/s) were observed. During the month of May, wind speed varied between 0 and 6.5 m/s and high levels of ozone were associated when wind speed ranged from 2 to 5 m/s. Vertical profile of ozone (MERRA 5.2.0, <https://giovanni.sci.gsfc.nasa.gov/giovanni/>) from 975 to 500 hPa also showed high levels on 7th and 8th May as compared to consecutive days. However, all the trajectories during the episodic event were within boundary layer and potential vorticity (<https://giovanni.sci.gsfc.nasa.gov/giovanni/>) was less than 1.2 PV (1 PV = $10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ K kg}^{-1}$) at all pressure levels (300–800 hPa), which suggest no vertical transport during the event. Earlier studies have suggested that potential vorticity (PV) greater than 1.5 PV in the troposphere is an indicator of stratospheric subsidence (Lai *et al.* 2011).

Air-mass trajectory analysis of 25% of days with high ozone and 25% of normal days was performed to elucidate the effect of wind pattern during the episodic event. The analysis was done using Geographical Information System (GIS) based

Figure 6. Diurnal variation of ozone, NO_x and wind speed during 5–11 May 2013.

Trajstat software (Wang *et al.* 2009). The meteorological files for running the model were extracted from GDAS archive at NOAA ARL ($0.5 \times 0.5^\circ$). 123 episodic days and 168 normal days were identified during May 2012–May 2013. The days when hourly ozone exceeded 90 ppb were considered as episodic days, however, when hourly ozone was below and close to 75 ppb were considered as normal days. Therefore, 31 episodic days and 42 normal days' air-masses are shown in figure 7(a and b). It is evident from the figure that wind directions were quite different during episodic and normal days. During episodic days, most of the air-masses were continental in nature and from north, northwest and central Indian region, however, during normal ozone days, most of the air-masses were marine in origin.

4.6 Surface ozone and respirable fine particles ($\text{PM}_{2.5}$)

The average $\text{PM}_{2.5}$ mass concentration was $93.9 \mu\text{g m}^{-3}$, maximum levels were observed in December ($218.6 \mu\text{g m}^{-3}$), while minimum in July

($25.7 \mu\text{g m}^{-3}$; figure 8a). In most of the months, the mass concentration was above NAAQ (National Ambient Air Quality) standard value, which is $60 \mu\text{g m}^{-3}$ (CPCB 2009) for 24 hr. The elevated levels observed in January (winter season) may be due to additional emission sources (increased biomass, coal and fossil fuel combustion) and stable meteorological conditions, which favour the ambient particles to remain suspended in the atmosphere. In monsoon months, heavy rainfall caused the removal of particulate matter by wet scavenging.

Aerosol can affect O_3 concentration because (a) aerosols can absorb or scatter a fraction of solar radiation causing change in photolysis rates, and affect O_3 formation (Jacobson 1998; Castro *et al.* 2001; Li *et al.* 2011); (b) aerosols can influence the tropospheric trace gas chemistry by providing surface for heterogeneous chemical reactions. Heterogeneous reactions occurring on the aerosols surface may affect trace gases concentrations (Jacob 2000; Xu *et al.* 2012). Xu *et al.* (2012) reported that heterogeneous reactions affect O_3 formation by (i) disturbing the radical and NO_x cycles and

Figure 7. Air mass back trajectories during (a) 25% of high ozone days and (b) 25% of normal day.

Figure 8. (a) Monthly variation of $PM_{2.5}$ and regression analysis between (b) $PM_{2.5}$ and O_3 , (c) O_3 and solar radiation, and (d) solar radiation and $PM_{2.5}$.

(ii) direct removal of O_3 by aerosols. Disturbance of radical and NO_x cycles include heterogeneous reactions with three species namely: NO_2 , N_2O_5 , and NO_3 . NO_2 heterogeneous reaction prevails where NO_x concentration is high and it produces HONO and HNO_3 . HONO produces OH° radicals by photolysis and adds more new radicals to the radical cycle. These radicals are responsible for initiation of O_3 formation and are predominant in urban areas. However, when NO_x concentration is low (NO_x -sensitive regime as in present site), the three heterogeneous reactions could proceed at a comparable rate, and the N_2O_5 heterogeneous reaction could have a relatively large effect on the NO_x cycle. HNO_3 is formed as a result of N_2O_5 and NO_3 heterogeneous reaction leading to direct removal of NO_x , causing a significant decrease in O_3 concentration (Xu *et al.* 2012; figure 9).

Partial Pearson correlation analysis was performed to elucidate the effect of $PM_{2.5}$ on ozone levels. For the analysis, ozone was considered as a dependent variable, solar radiation (SR) as an independent variable and $PM_{2.5}$ as a controlling variable. For zero order correlation ($PM_{2.5}$ was not controlling), ozone showed significant positive correlation with SR ($r = 0.52$, $p < 0.001$) and negative correlation with $PM_{2.5}$ ($r = -0.65$, $p < 0.001$), while $PM_{2.5}$ showed significant negative correlation with SR ($r = -0.46$, $p < 0.001$). However, the Pearson correlation coefficient between ozone and SR reduced to $r = 0.32$ ($p < 0.05$) when $PM_{2.5}$ act as a control or mediator factor, therefore, in presence of $PM_{2.5}$ correlation between SR and ozone is reduced. According to Dickerson *et al.* (1997),

particulate matter of absorptive nature (mineral dust and soot) may reduce UV radiations, and Indian aerosols have high loadings of mineral dust and soot particles (Pipal *et al.* 2014), therefore, they may lead to decreased ozone levels.

From the regression equations (figure 8a–c), the loss of O_3 through $PM_{2.5}$ due to their effect on SR can be calculated. From equation (1), $10 \mu g m^{-3}$ increase in $PM_{2.5}$ results in the decrease of $1.96 \mu g m^{-3}$ of ozone. This decrease involves both decreases in the photochemical formation of ozone (decrease in SR results in the decrease in O_3 formation) and loss through heterogeneous reactions. $10 W m^{-2}$ increase in solar radiation results in $0.84 \mu g m^{-3}$ increase in ozone levels (equation 2). Similarly, from equation (3), it is evident that $10 \mu g m^{-3}$ increase in $PM_{2.5}$ results in the decrease of $8.78 W m^{-2}$ of solar radiation, which causes the decrease of $0.74 \mu g m^{-3}$ of ozone levels (equations 2 and 3). This decrease was due to the decrease in solar radiation caused by $PM_{2.5}$.

$$O_3 = -0.196 PM_{2.5} + 104.3 \quad (1)$$

$$O_3 = 0.084 SR + 47.3 \quad (2)$$

$$SR = -0.878 PM_{2.5} + 477.8 \quad (3)$$

However, as the total decrease of ozone due to $PM_{2.5}$ was $1.96 \mu g m^{-3}$, therefore, $1.22 \mu g m^{-3}$ decrease may be due to heterogeneous reactions (after subtracting loss through decrease in SR from total loss).

5. Conclusions

The study investigates the complex chemistry of surface O_3 and NO_2 at a sub-urban site, Dayalbagh, Agra for the period May 2012–May 2013. The salient points of the study are as follows:

- The diurnal variation was characterized by minimum O_3 concentration during the early morning or night hours (20.3 ± 9.6 ppb) and maximum value at around noontime (67.2 ± 27.9 ppb) coinciding with intense solar radiation.
- O_3 showed a distinct seasonal variation on the diurnal scale with the highest amplitude in summer (79.7 ± 15.9 ppb), followed by post-monsoon (73.0 ± 9.5 ppb), winter (58.9 ± 20.5 ppb) and lowest in monsoon (32.0 ± 5.1 ppb). High levels in summer season were mainly attributed to intense solar radiation and high temperature, which favour photochemical generation of O_3 .

Figure 9. A schematic representation of three heterogeneous reactions at the surface of aerosols.

- The positive rate of change of O_3 was maximum in April (16.3 ppb/hr), while minimum in August (1.1 ppb/hr), the negative rate of change of O_3 was maximum in December (−13.2 ppb/hr) and minimum in July (−1.1 ppb/hr). The average rate of change of O_3 (−6.9 ppb/hr) during evening hours was lower than their respective production rate (7.9 ppb/hr) during morning hours. This has been attributed to slower titration of ozone by NO during the late evening.
- The O_3/HNO_3 ratio was used an indicator to assess O_3-NO_x-VOC sensitivity. This value is above the threshold value in summer, post-monsoon and winter indicating the present site was NO_x sensitive.
- A high ozone episode was observed during 6–10 May, 2013 which was attributed to photochemistry and transport using meteorological parameters.
- Loss of ozone through $PM_{2.5}$ was calculated using regression analysis and it was estimated that $10 \mu g m^{-3}$ increase in $PM_{2.5}$ results in decrease of $0.74 \mu g m^{-3}$ ozone through reduction in solar radiation and $1.22 \mu g m^{-3}$ of ozone through heterogeneous reactions.

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