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Impact of Nitrogen Oxides, Volatile Organic Compounds and Black Carbon on Atmospheric Ozone Levels at a Semi Arid Urban Site in Hyderabad

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ABSTRACT

The surface level ozone (O_3), nitrogen oxides (NO_x = NO_2 + NO), volatile organic compounds (VOCs), black carbon (BC) and meteorological parameters were continuously monitored for the period of one year (2010) at an urban site in Hyderabad using different trace gas monitors. The local emissions and meteorology have been found to play a significant role in diurnal variations of O_3. The average peak time mixing ratios of O_3 were observed in the range of 23 ± 8 to 67 ± 13 ppbv. Diurnal-seasonal variation of O_3 and its precursors were also reported. The observed O_3 concentrations were higher during the day than in the night. Maximum O_3 concentrations in the three seasons i.e., summer, winter and monsoon were 56 ± 14 ppbv, 50 ± 9 ppbv, and 28 ± 10 ppbv, respectively. Weekday/weekend variation of O_3 and its precursors were studied during the three seasons. High O_3 concentrations were observed on weekends compared to weekdays, however, NO_x and BC levels were found low during weekends. The weekend effect of O_3 was high during winter. The annual average afternoon peak time O_3 levels on weekends were 11% higher than the weekday concentrations. Weekday/weekend variations of NO_x at morning traffic rush hour were 14%, 9% and 8% in winter, summer and monsoon, respectively. The annual mean of NO_x and BC concentrations at weekend were observed to be lower than weekday about 10% and 9% respectively. VOC/NO_x ratio is more (5) during weekend than weekday (4) which resulted in enhanced O_3 formation.

***Keywords*:** Trace gas; Ozone; Volatile organic compounds; Black carbon; Meteorology and oxides of nitrogen.

INTRODUCTION

Total energy consumption in Asia was more than doubled from 1980 to 2003 causing a rapid growth in emissions of BC, CO, VOCs, sulphur dioxide (SO_2), and NO_x. Asian total emissions of SO_2, NO_x, and NMHCs were predicted to increase by 22%, 44%, and 99% respectively over 2000 levels (Ohara *et al*., 2007).

Ozone is a secondary air pollutant formed by photochemical reaction of the precursor pollutants and primary oxidant to other highly reactive trace gases (Bauguitte *et al*., 2010). Higher tropospheric concentrations of O_3 may cause respiratory problems (Gielen *et al*., 1997; Romieu *et al*., 1997; Lin *et al*., 2004), and may reduce the crop yield (Dingenen *et al*., 2009; Avnery *et al*., 2011). It is very important to identify the main sources of O_3 formation and quantify the contribution of each source to reduce ambient concentrations of O_3. Formation of O_3 in the atmosphere is mainly due to photochemical reaction of NO_x, VOCs and CO in the presence of solar radiation (Crutzen *et al*., 1999). Variation of O_3 concentration depends on several meteorological parameters viz., temperature, relative humidity, solar radiation, wind speed and wind direction (Lin *et al*., 2007). Hence, understanding the behavior of O_3 in the urban atmosphere is very complex. O_3 in the troposphere is produced by the photolysis of NO_2 in the presence of solar radiation, and inversely it is being destructed by titration with NO, as given below (Lal *et al*., 2000).

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$
$$O_3 + NO \rightarrow O_2 + NO_2$$

The phenomenon of elevated O_3 concentrations on weekend compared to weekdays in urban areas is known as the "*weekend effect*". The higher levels of O_3 concentrations were observed on weekends even though the emissions of O_3 precursors were lower on weekends than on weekdays. Different hypotheses were proposed to explain the cause for the weekend effect of O_3 (Bronnimann and Neu, 1997; Fujita *et al*., 2003; Murphy *et al*., 2007). However, till date no justified explanation was given for the O_3 weekend

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effect. Reduced levels of NO_x emissions in the weekend are the most common reason for weekend effect of O_3 (Sadanaga *et al*., 2008). Moderate NO_x concentrations on weekends are suitable for increased photochemical production and less O_3 titration compared to weekdays (Debaje and Kakade, 2006). Han *et al*. (2011) also observed high weekend levels of O_3 due to less consumption by NO.

It was reported that VOC/NO_x ratio also plays an important role on weekend effect (Jenkin *et al*., 2002; Atkinson-Palombo *et al*., 2006; Sadanaga *et al*., 2012).Vehicular traffic is the main source for VOCs and NO_x where, light-duty vehicles (LDV) produce more VOC emissions, while diesel-powered heavy-duty trucks (HDT) are main sources of NO_x emissions (Marr and Harley, 2002a; Gao and Niemeier, 2007). VOC sensitivity towards the photochemical production of O_3 combined with lower emission of NO_x on weekend causes weekend O_3 effect (Marr and Harley, 2002b; Qin *et al*., 2004; Blanchard and Tannenbaum, 2006). However, weekend NO_x emissions were very less than weekday emissions, while there was no much difference in VOCs weekend emissions (Jimenez *et al*., 2005). Dreher and Harley (1998); Marr and Harley (2002a) also supported that the HDT traffic on highways was 70–80% lower on weekends compared to weekdays, while LDV traffic was only 10% lower. Less scatter of sunlight due to lower fine particle concentrations might be another reason for enhanced levels of O_3 formation on weekends (Dreher and Harley, 1998; Qin *et al*., 2004). Lonati *et al*. (2006) showed that PM_{10} concentration on weekend was about 17% lower than the mean value of the week days in winter and 25% lower in summer. However, overnight carryover of precursors did not show any significant effect on weekend O_3 concentrations. In this study, an attempt has been made to evaluate the variation in diurnal weekend/weekday pattern of O_3 with change in the diurnal concentrations of NO_x, BC and VOCs and its impact on O_3 formation, during all the seasons in a year, were discussed.

SITE DESCRIPTION AND CLIMATE

The experimental site was located at Tata Institute of Fundamental Research- National Balloon Facility (TIFR-NBF, 17.47°N and 78.58°E), Hyderabad (Fig. 1). Hyderabad is situated in the Deccan plateau and has an average elevation of about 536 m above mean sea level. Hyderabad is a wide urban location covering an area of 217 sq. km. As per census 2011, population of Hyderabad is more than seven millions with the density of 18,480 per square km. The number of vehicles in the city was 18.47 lakhs by the end of year 2007. Hyderabad city comprises of many industrial development areas. The site is surrounded by many industries such as Electronics Corporation of India Limited (ECIL), Hindustan Cables Limited (HCL), Nuclear Fuel Complex (NFC), petroleum storage containers, bottling units of Hindustan Petroleum Corporation Limited (HPCL), Bharat Petroleum Corporation Limited (BPCL) in the south, south-east and south-west directions.

Hyderabad has a unique combination of wet and dry climate that limits on a hot semi-arid climate with hot summers from March to early June months, the monsoon season from late June to October and a pleasant winter observed from November to February. During the months of December and January, the nights become quite cool in and around Hyderabad city, in monsoon moderate average rain fall of 810 mm observed in every year. The air masses during monsoon months arrive from southwest direction while in the other seasons wind flows from southeast direction. The maximum air temperature was observed in May (summer) and minimum temperature was observed in December (winter).

MEASUREMENT TECHNIQUES AND DATA ANALYSIS

The trace gases in ambient air were measured simultaneously for every 5 min interval with Thermo Scientific instruments. These measured values were averaged to attain daily and monthly concentrations. Auto-sampling was made at 10 meters elevation above the ground level. Continuous measurements of O_3 concentration were done by using Model 49*i*; Thermo Scientific, USA. The operating principle is that, O_3 molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light absorbed is directly related to the O_3 concentration as described by the Beer-Lambert law. Lower detection limit of the analyzer is 1 ppbv with the response time of 20 seconds. The O_3 analyzer is calibrated by the insitu generation of O_3 using O_3 generator.

NO_x measurements were done by using Model 42*i*; Thermo scientific, USA. The analyzer works on the principle that NO and O_3 react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. To quantify the NO_2 concentrations it must be transformed into NO before involving in chemiluminescent reaction. NO_2 was converted to NO by molybdenum heated to about 325°C. Lower detectable limit of NO_x analyzer is 0.40 ppbv; with response time 40 seconds. Zero and span calibration of gas analyzers were performed by Thermo scientific multigas calibrator (Model 146*i*) using NIST traceable standard gas.

An Aethalometer (Model AE-21 of Magee Scientific, USA) was used to measure BC concentrations, which measures the decline of light transmitted through a quartz filter tape on which the ambient particles are imposed. The reduction in the transmission consequent to the collection of particles was calibrated in terms of the mass concentration of BC. Measurement of BC mass concentrations was done in the wavelength range of 370 to 950 nm. BC mass concentration measured at 880 nm is considered to represent true value of BC in the atmosphere as BC is the principal absorber at this wavelength. Data of meteorological parameters such as temperature, relative humidity, wind speed and direction were collected from Automatic Weather Station (AWS).

To determine VOCs in ambient air, samples were collected in 500 mL glass air sampling unit at TIFR site and two traffic junctions Habsiguda and Tarnaka in Hyderabad. Air samples were transferred into an evacuated 250 mL stainless

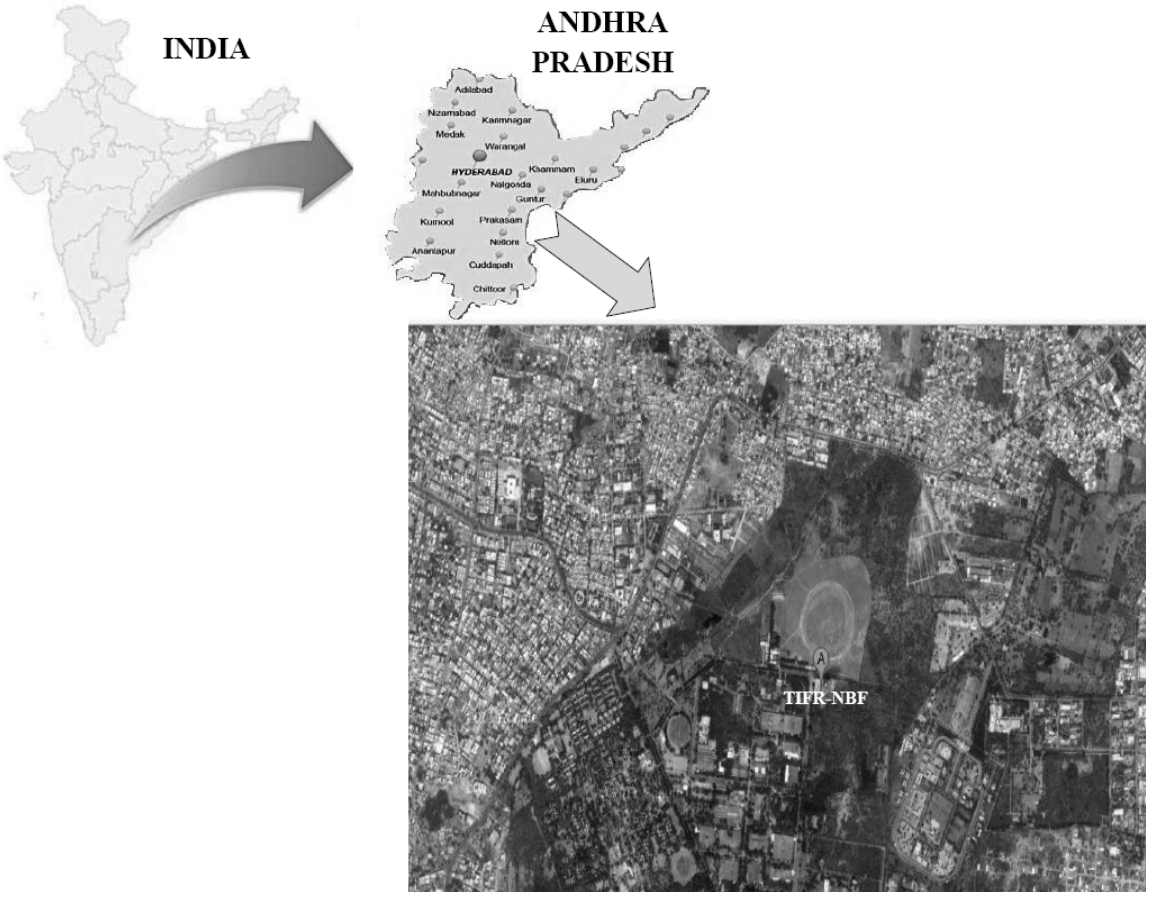

Fig. 1. Geological topography of experimental site TIFR–NBF (Balloon-A) and Hyderabad.

steel canister. The canister is connected to the 8-valve port (V_1), a U type column (25 cm long with 6.3 mm outer diameter) filled with glass beads of 60/80 mesh is connected between one port of V_1 with another 6-valve port (V_2). The air from the canister was loaded into the U-column and pre-concentrated for a pre-determined time under cryogenic conditions by using liquid nitrogen. After pre-concentration the column was kept under isolated condition and heated with warm water. The volatile desorbed gases are injected into GC (Gas chromatograph) for analysis. Sample loading, isolation and injection were carried out by operating V_1 and V_2 valves. VOC's (ethylene, acetylene, ethane, propane, n-butane, i-pentane and n-pentane) were analyzed using GC (Schimadzu GC-17A) equipped with Flame Ionisation Detector (FID) with Al_2O_3/KCl, PLOT capillary Column (30 M × 0.53 mm). High pure IOLAR grade nitrogen gas (7 mL/min) was used as carrier gas, H_2 and Zero air as fuel and oxidative gases, respectively. The column oven temperature was ramped from 40°C to 180°C. Initially 40°C was maintained for the first 5 minute; afterwards the temperature was increased at a rate of 5 °C/min until it reaches 120°C and kept at this temperature for 5 min. In the final step the temperature was increased to 180°C at a rate of 25 °C/min and then held at 180°C till the end of the analysis. The identity of each peak, by noting their retention times, was determined by injecting pure samples of the individual gases as well as mixures of NIST traceable Linday spectra standards (USA). A calibration graph of area versus concentration was drawn for the quantification of each analyte.

RESULTS AND DISCUSSION

Diurnal and Seasonal Variations of Ozone

Concentrations of BC, O_3 and its precursor NO_x were monitored continuously during different seasons to compare weekend/weekday variations. Formation of O_3 in urban area mainly depends on the emission levels of NO_x. Vehicular traffic is the major source of NO_x emission at the urban site. Diurnal profile of O_3 (Fig. 2) indicate that O_3 concentration starts increasing after the sunrise reaching to a peak value by noon time and thereafter dropped by the evening. The increased midday concentrations of O_3 were due to photochemical oxidation of precursors in the presence of sufficient NO_x concentration and increased boundary layer height. The increase in height of the boundary layer resulted in O_3 mixing due to the thermal stratification and convective heat transfer to the surface from air at greater altitudes. Since, O_3 concentrations are usually associated with temperature and solar radiation (Dawson *et al*., 2007; Stathopoulou *et al*., 2008); noon time O_3 concentration was observed to be higher when temperature and solar radiations attain peak value (Fig. 3 and Fig. 4). The relationship between O_3 concentrations, its precursors and meteorological conditions were examined by Pearson's correlation (Table 1). O_3 showed

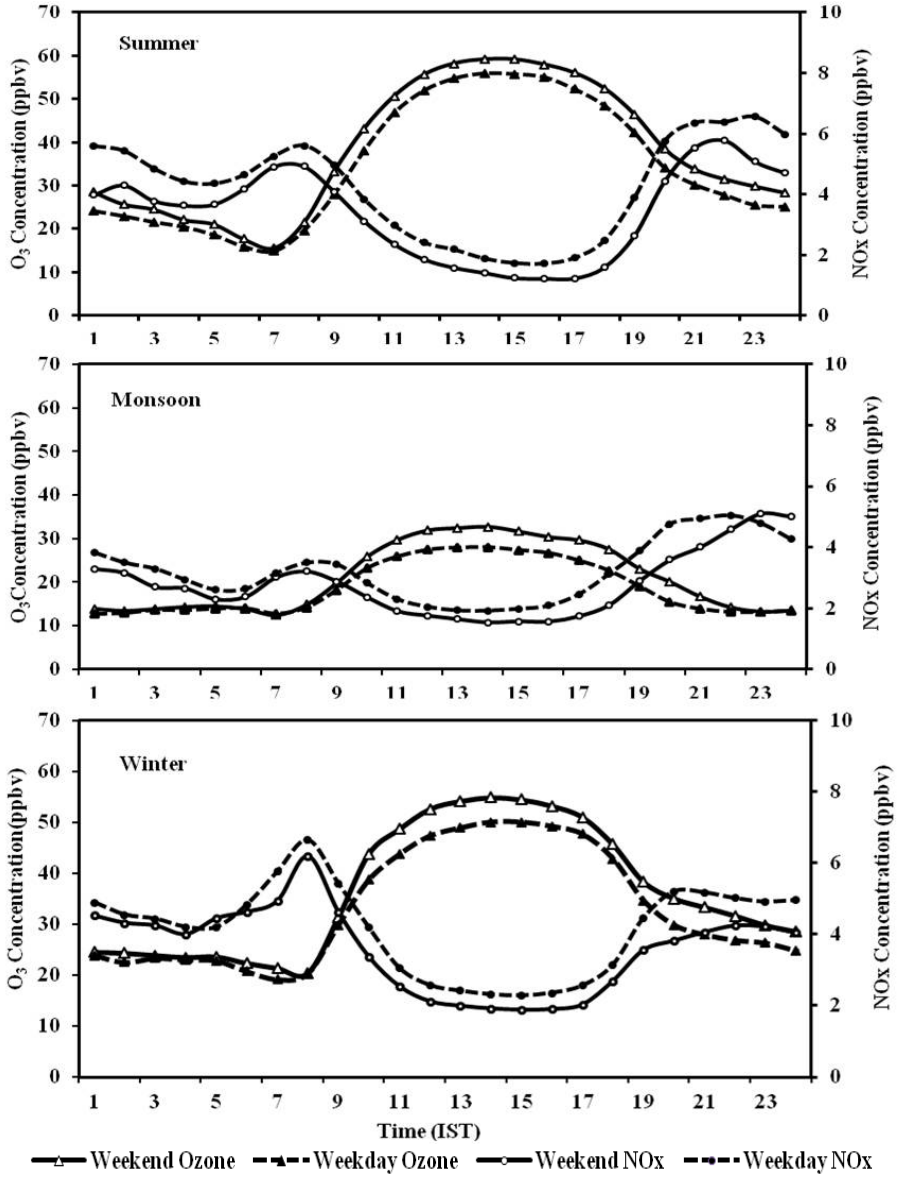

Fig. 2. Diurnal variations of O_3 and NO_x concentrations on weekday and weekend during different seasons.

positive correlation with temperature and solar radiation whereas RH, NO_x and BC correlated negatively. The low values of O_3 during late evening and night might be associated with the combined effect of chemical loss by NO titration and suppressed boundary layer. There is no possibility for further photochemical oxidation to form O_3 at night due to lack of sunlight. Month wise variation profile of O_3 from January to December is shown in Fig. 5. It reveals that highest peak of O_3 concentrations was observed in the month of March about 67 ± 13 ppbv and gradually decreased to a lower value (23 ± 8 ppbv) in the monsoon month of September. Higher concentrations of O_3 in summer were caused by regional photochemistry favored by strong solar radiation and higher temperatures (Fig. 3 and Fig. 4). The wet surface deposition of air pollutants by rain and inadequate availability of solar flux, high relative humidity are some of the factors for lower monsoon O_3 concentrations observed during monsoon than in summer and winter. Despite that weekend emissions of NO_x were lower than weekday emissions, day time weekend O_3 levels were observed higher than the weekday concentrations during all the seasons. Similar weekend trend was observed during winter and monsoon periods also, whereas in summer the effect was relatively less. Weekend O_3 was higher than weekday in all the seasons throughout the year except few weeks. Diurnal variations of O_3 concentrations on weekday and weekend during different seasons were depicted in Fig. 2. The highest mean O_3 concentrations observed, in afternoons of summer, during weekend and weekdays were about 59 ± 13 ppbv and of 55 ± 14 ppbv respectively. Similarly variation of O_3 55 ± 5 ppbv and 49 ± 9 ppbv in the afternoon during weekend and weekday was recorded during winter period whereas lowest weekday peak level of 28 ± 10 ppbv O_3 was observed in monsoon with 32 ± 12 ppbv on weekends. The lowest weekday/weekend O_3 concentration difference of 1.1 ppbv was observed in June while higher variation 8.1

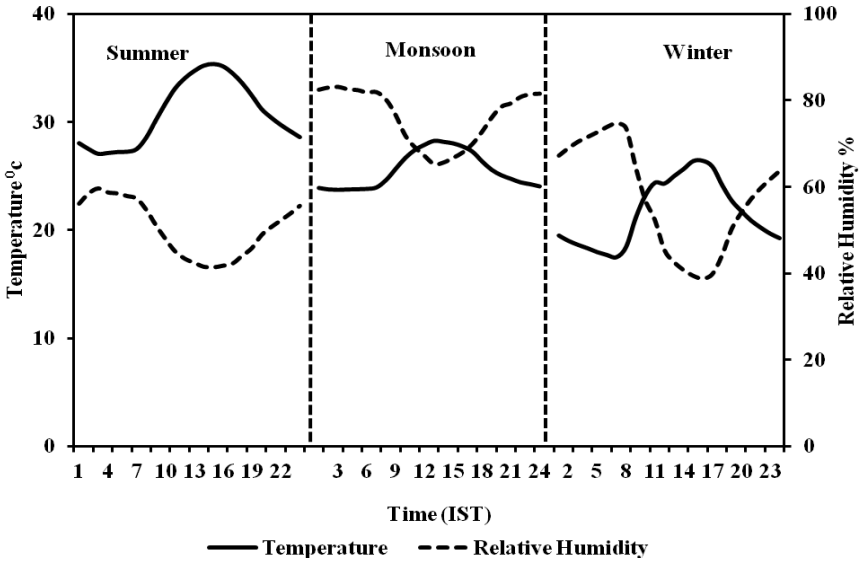

Fig. 3. Diurnal variations of temparature and relative humidity during different seasons in 2010.

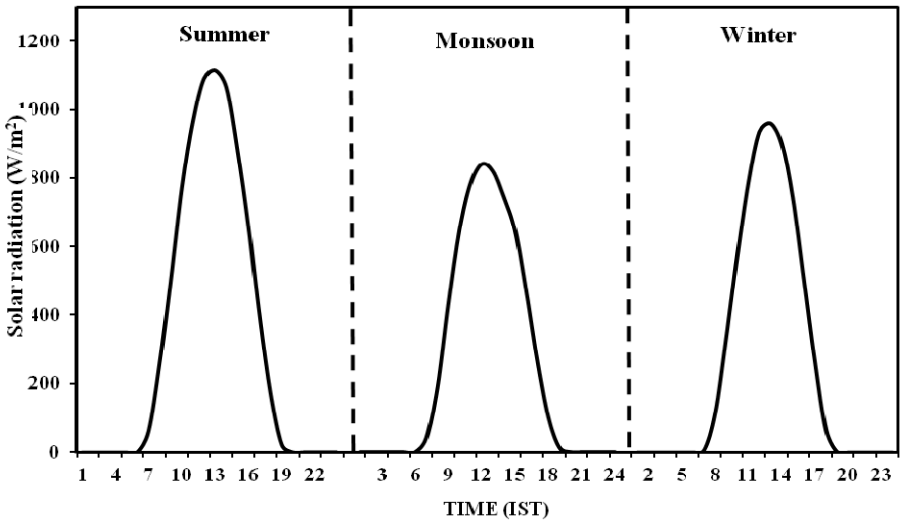

Fig. 4. Diurnal variations of solar radiation during different seasons in 2010.

Table 1. Pearson correlation matrix of O_3 levels with different variables.

Variables	Summer	Monsoon	Winter
NO_x	–0.353*	–0.260**	–0.461**
SR	0.517**	0.591**	0.644**
T	0.449**	0.547**	0.503**
RH	–0.082	–0.657**	–0.618**
WS	0.069	0.078*	0.508**
BC	–0.240*	–0.254**	–0.445**

* Values with $p < 0.005$; ** values with $p < 0.001$.

ppbv was observed in July (Fig. 6). However, winter showed relatively more weekday/weekend concentration variations than summer and monsoon.

Diurnal-Seasonal Variations of NO_x, VOCs and Its Impact on Ozone Weekend Effect

The studies indicated that the O_3 weekend effect mainly depend on the variation of NO_x emission levels. Diurnal variations of NO_x concentrations showed two peaks (one in the morning and the other in late evening traffic rush hours). The highest morning peak concentration of NO_x (6.5 ± 4 ppbv) was measured in winter followed by summer (5.3 ± 2 ppbv) and monsoon (3.5 ± 2 ppbv). The high mixing ratios of NO_x during the morning and evening hours were mainly attributed to the vehicular emissions (Harley *et al*., 2005). Vehicular emissions in the evening hours get trapped in surface levels due to decreased height of boundary layer till the early morning hours. Reduction of NO_x during midday was caused by combined effect of photochemical oxidation of precursors to form O_3 and dilution of NO_x due to increased boundary layer as well as reduced traffic during afternoon time. Fig. 5 describes the month wise variations of NO_x from January to December. Highest peak time concentration of NO_x was observed in March (8 ± 3 ppbv)

and gradually decreased to the lower value (3 ± 1 ppbv) in the month of July (monsoon).

Contrary to ozone weekend effect, lower levels of NO_x and BC were observed on weekend than weekdays attributing to the reduced traffic on weekends compared to weekdays. Results of NO_x showed that during the morning peak hour weekday/weekend difference was 9% in summer, 8% in monsoon and 14% in winter.

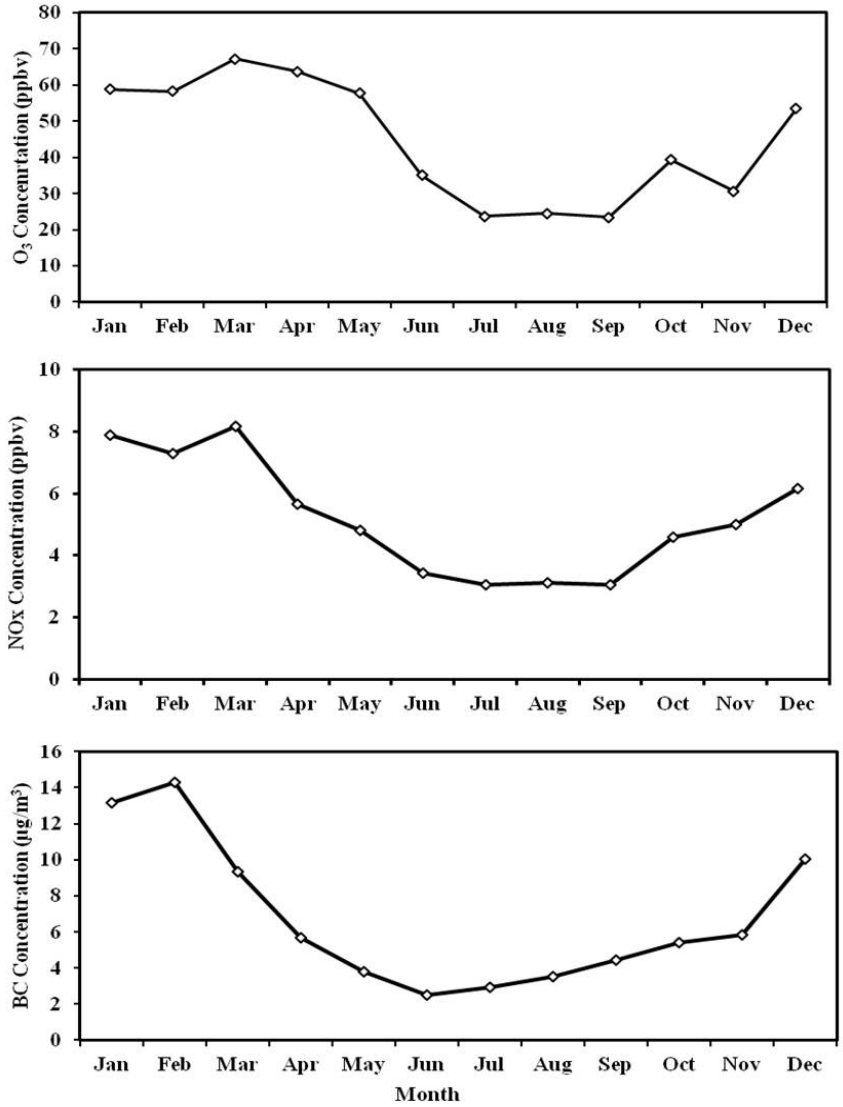

Fig. 5. Monthly mean peak time concentrations of O_3, NO_x and BC in 2010.

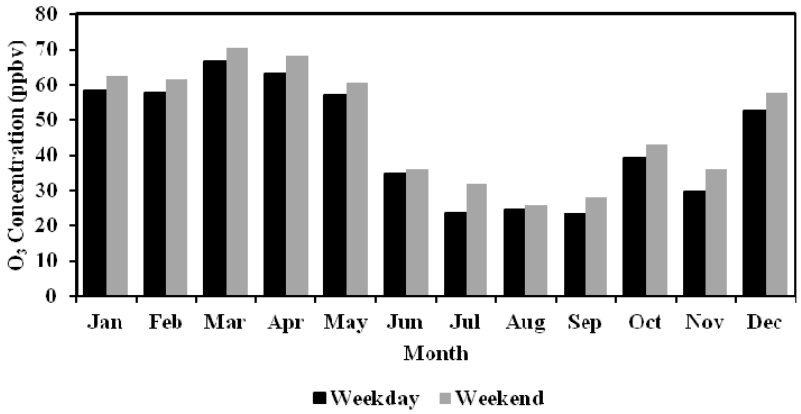

Fig. 6. Weekday/weekend differences of O_3 during different months.

Emission levels of VOCs for the year 2010 at three different junctions in Hyderabad are reported in Table 2. The results indicate high emissions at traffic junctions than the experimental (TIFR) site. As the measurement site being away from these traffic junctions, pollutants are getting diluted and hence, showing relatively low concentration. Seasonal mean O_3 and VOC concentrations for all seasons are summarized in the Table 3. The data showed significant seasonal variation in the concentration of O_3 and VOCs. Mean concentration of VOCs in winter was relatively higher followed by summer and monsoon. Even though there is no much seasonal variability in emission sources, the variation in VOC concentration during different seasons is attributed to the OH radical chemistry with hydrocarbons. The loss rate of VOCs through the reaction path with hydroxyl ($OH^{\bullet}$) (Eq. (1)) is maximum in summer (Liakakou *et al*., 2009), thus exhibiting minimum VOC concentration than in other seasons due to the formation of O_3. The observed weekday/weekend variations in the emission of VOCs (C_2-C_5) at TIFR site at different time intervals were summarized in Fig. 7. The average weekend emissions of VOCs observed to be 16% higher than weekdays. The average weekend/ weekday differences are 26% for ethylene, 45% (acetylene), 47% (ethane), 61% (propane), 15% (n-butane), 6% (i-pentane), 5% (n-pentane). VOC/NO_x ratio on weekend (5) is greater than weekday (4) due to the increased emissions of hydrocarbons and decreased emissions of NO_x compare to weekdays. Increased LDV traffic, commercial use of lawn and garden equipment, some residential activities during weekends might be the reason for high emissions of hydrocarbon.

The chemistry of hydrocarbons plays an important role on formation of O_3. Oxidation of hydrocarbons in the atmosphere is primarily initiated by reacting with $OH^{\bullet}$ to form alkyl peroxy radicals and hydroperoxy radicals.

$$RCH_3 + OH^{\bullet} \rightarrow RCH_2^{\bullet} + H_2O \quad (1)$$

$$RCH_2^{\bullet} + O_2 \rightarrow RCH_2O_2^{\bullet} \quad (2)$$

$$RCH_2O_2^{\bullet} + NO \rightarrow RCH_2O^{\bullet} + NO_2 \quad (3)$$

$$RCH_2O^{\bullet} + O_2 \rightarrow RCHO + HO_2^{\bullet} \quad (4)$$

Peroxy radicals produced in Eq. (2) and Eq. (4) continue to react with NO to form NO_2.

$$HO_2^{\bullet} + NO \rightarrow OH^{\bullet} + NO_2 \quad (5)$$

NO_2 formed through the series of intermediate reactions in atmosphere viz. Eqs. (3) and (5) liberates oxygen atom (O) which helps in the formation of O_3 by the following reactions.

$$NO_2 + h\nu \rightarrow NO + O \quad (6)$$

$$O + O_2 \rightarrow O_3 \quad (7)$$

NO formed in Eq. (6) titrates the O_3 to form oxygen molecule.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (8)$$

It is understood from Eqs. (7) and (8), that the formation and destruction of O_3 takes place simultaneously, indicating the probability of no net O_3 formation at steady state. However, NO is also getting oxidized by reacting with peroxy radicals (Eqs. (3) and (5)) to form NO_2, resulting in formation of O_3. In presence of relatively high concentration of VOCs, the probability for photochemical oxidation of NO to NO_2 will be higher, thus NO does not contribute to titration reaction resulting in high O_3 levels. In case of low VOCs concentrations the converse will occur i.e., once the availability of hydrocarbons is not much to photo oxidize NO, that result in more O_3 titration. Thus, VOC/NO_x ratio is an important criterion for O_3 formation which would result in increased photochemical oxidation. Relatively high VOC/ NO_x ratio observed in weekends than in weekdays resulted in higher weekend O_3 concentrations at this site. Low NO_x

Table 2. Emissions of VOCs at different locations in Hyderabad: TIFR, Tarnaka and Habsiguda.

Constituents	Annual Avg. Concentration of VOCs in ppbv		
	Tarnaka	Habsiguda	TIFR
Ethylene	3.12	3.76	3.09
Acetylene	28.28	10.05	2.62
Ethane	60.98	17.39	28.35
Propane	42.15	22.70	3.50
n-Butane	36.97	13.19	2.44
i-Pentane	34.05	7.83	7.71
n-Pentane	229.33	107.81	116.65

Table 3. Concentrations levels of O_3 and VOCs during different seasons at TIFR site in the year 2010.

Pollutants / Seasons	VOCs (ppbv)			Ozone (ppbv)		
	Avg	Max	Min	Avg	Max	Min
Summer	14 ± 7	26 ± 20	8 ± 5	35 ± 14	56 ± 14	14 ± 3
Monsoon	11 ± 2	14 ± 9	9 ± 7	18 ± 6	29 ± 7	12 ± 6
Winter	19 ± 9	33 ± 21	10 ± 9	33 ± 11	50 ± 13	19 ± 5

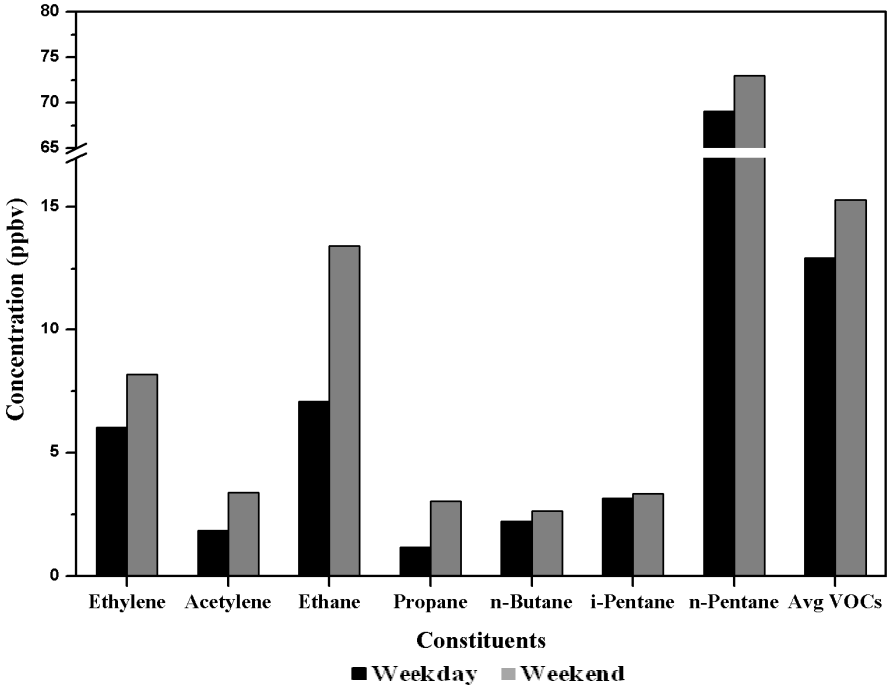

Fig. 7. Annual average weekday/weekend differences of volatile organic compounds (VOCs) in 2010 at TIFR.

concentrations levels led to high concentrations of O_3 on weekend; while, low concentrations of O_3 were observed during week days due to O_3 titration with NO.

Diurnal-seasonal Variations of BC and Impact on Ozone Weekend Effect

BC is a primary air pollutant, directly emitted to atmosphere by incomplete combustion of fossil fuels, industrial effluents and vehicular emissions. BC showed similar diurnal profile like NO_x. The diurnal variation of BC mass concentrations (Fig. 8) shows peak values during morning (08:00 h) and evening (21:00 h) traffic hours. The BC levels at midnight were less than the evening rush hours due to lack of anthropogenic emissions. Low levels of BC during afternoon were attributed to the increase in boundary layer height and low traffic density. BC mass concentrations were observed maximum during winter (10.3 ± 6 μg/m^3), minimum in monsoon (4.6 ± 2 μg/m^3) and moderate in summer (5.3 ± 3 μg/m^3). Winter concentrations were about two times higher than summer and monsoon. The observed highest mean concentration in winter was attributed to the trapping of air pollutants in the shallow boundary layer, while low values in monsoon were the scavenging effect of rainfall. Dispersion of BC aerosols caused by high convective activity might be responsible for relatively low concentrations during summer compared to winter. The morning traffic rush time emission of BC was recorded minimum in July (2.9 ± 1 μg/m^3), increased gradually and attained higher value in February (14.3 ± 8 μg/m^3). During the morning rush hours relatively large weekday/weekend difference of BC mass concentrations were observed in winter (11%) followed by summer (9%) and monsoon (8%). BC concentration showed an inverse profile (Fig. 8) to that of O_3 concentration. Relative high BC concentration in weekdays than in weekend might have contributed to the low O_3 concentration levels. The role of BC particles on the reduction of O_3 in troposphere was hypothesized (Fendal *et al*., 1995) using collision chemistry. The large concentration differences in BC (Fig. 8) as well as NO_x (Fig. 2) observed during winter in presence of solar radiation could have caused high weekend effect on O_3 when compared to summer and monsoon.

CONCLUSIONS

Weekday/weekend variation of O_3, NO_x, VOCs and BC were evaluated to study the ozone weekend effect during different seasons in Hyderabad. The results indicate that the concentration levels of O_3 were observed to be higher on weekend during all the seasons. Pronounced weekend effect of O_3 was observed in summer than winter and monsoon. Weekday/weekend variations in the emission of NO_x, BC and VOCs were playing an important role on weekend effect of O_3. Weekend emissions of NO_x and BC were lower due to reduced traffic density. The high VOC concentrations during weekends reduced the titration of O_3 by enhancing the photochemical oxidation of NO to NO_2 in presence increased VOCs/NO_x ratio, caused high levels of O_3 during weekends. Formation of O_3 was controlled by VOC emissions. The other reason for the enhanced O_3 formation on weekends can be attributed to the less absorbance of sunlight due to reduced BC particle emissions.

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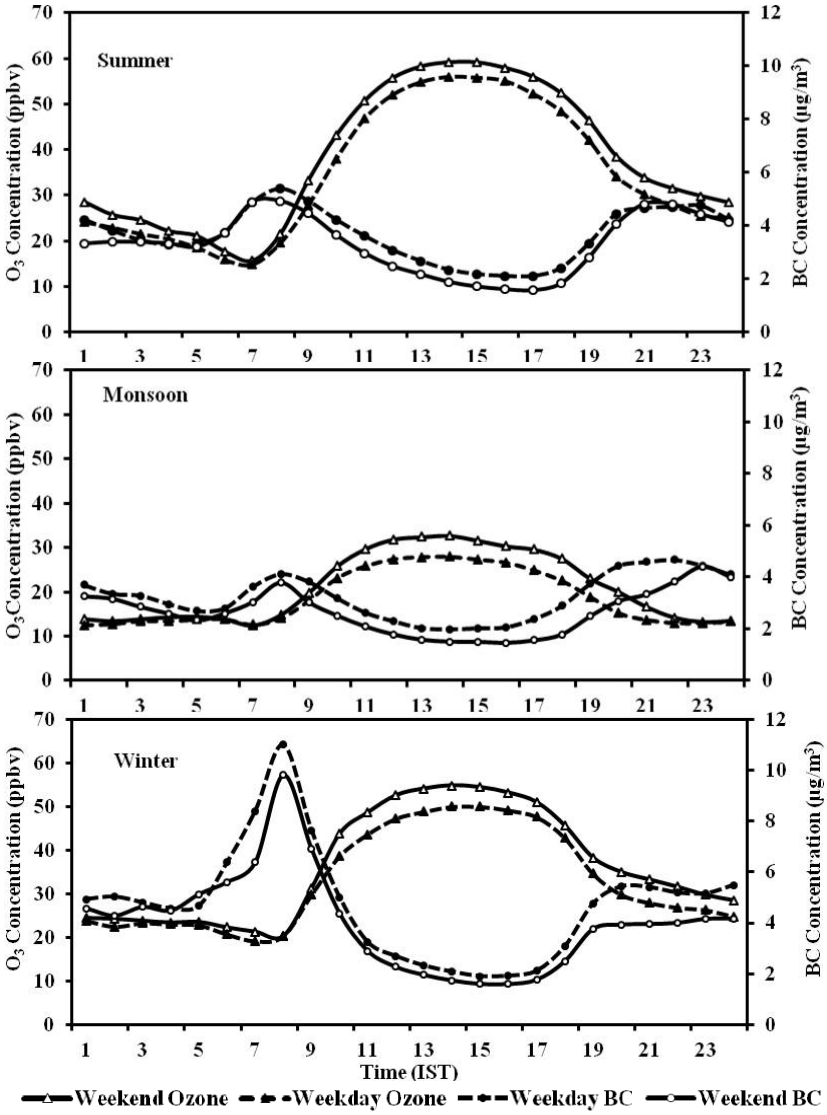

Fig. 8. Variations of BC and O_3 concentrations on weekday and weekend during different seasons in 2010.

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