Weekend Ozone Effect over Rural and Urban Site in India

S.B. Debaje[1]*, A.D. Kakade[2]

[1] *Indian Institute of Tropical Meteorology, Pune 411 008, India*
[2] *New Arts, Commerce and Science College, Parner 414 302, India*

Abstract

Weekend ozone effect studied over a tropical rural and urban site in India shows higher ozone (O_3) concentration on weekend compared to weekday. The weekend ozone effect was observed mostly during the summer and winter at the urban, and during summer season at the rural site. Decreased NOx emissions combined with VOC sensitivity on weekends appears to be the possible cause of the weekend ozone effect. The NOx concentration was low on weekend due to reduced commuter vehicular traffic emission. The results indicate nonlinear behavior in the chemistry of O_3 production over the tropical region.

Keywords: Surface ozone; Weekend effect; Photochemical production; NOx titration; Precursor gas emission.

INTRODUCTION

A phenomenon of higher ozone (O_3) concentration on weekend (Saturday to Sunday) compared to weekday (Monday to Friday) is referred to as the "weekend ozone effect," despite the lower emission of anthropogenic precursor gases on weekend. Weekend O_3 effect has been reported in some areas in America since the 1970s (Elkus and Wilson, 1977). The weekend O_3 effect has been observed over mid- and high-latitude environments containing mostly nitrogen oxides (NOx), NOx-saturated or volatile organic compounds (VOC), VOC-sensitive (Blanchard and Fairley, 2001; Beaney and Gough, 2002; Marr and Harley, 2002; Qin *et al*., 2004). Altshuler *et al*. (1995) suggested that different dropped rates for NOx and VOC emission on weekend is a major cause of the weekend O_3 effect in California. Dreher and Harley (1998) considered that different heavy-duty diesel truck activity on highways between weekdays and weekends caused

*Corresponding author. Tel.: 020-25893600 Ext. 349 , Fax: 020-25893825

E-*mail address:* debaje@tropmet.res.in

different reductions for NOx and VOC responsible for weekend O_3 effect. Vukovich (2000) proposed that a larger amount of previous-day carryover ozone was responsible for the higher weekend ozone. Marr and Harley (2002a, b) proposed that less absorption of sunlight due to lower fine-particle concentrations on weekend, resulting in enhanced ozone formation, might be a cause for the weekend ozone effect. Qin *et al*. (2004) suggested that VOC sensitivity combined with a decrease of NOx emissions on weekend was a cause.

Blanchard and Fairley (2001) based suggested criteria for occurrence of weekend O_3 effect on differences between weekend and weekday ozone. If that difference is less than 5 ppbv, no weekend O_3 effect is observed. A difference of 5-15 ppbv is considered a moderate weekend O_3 effect, and intense weekend O_3 effect is above 15 ppbv. However, the mechanisms for the weekend effect on O_3 formation are still not well understood.

Asia, particularly India, is considered to be NOx-limited for photochemical production of O_3 (Berntsen *et al*., 1996). Road vehicular traffic is a dominant anthropogenic emission source of ozone precursor, particularly NOx (Garg *et al*., 2001). The diurnal and seasonal variation of O_3 is controlled by photochemical production of O_3 which is related to NOx concentration (Lal *et al*., 2000; Naja and Lal, 2002; Debaje *et al*., 2003). However, O_3 concentration is higher on weekend than weekday in spite of low vehicular commuter traffic emission of NOx over the tropics. In this study, the possible cause for occurrence of the weekend O_3 effect over the Indian region is discussed.

METHODOLOGY

Measurement site

Measurements of O_3 were carried out at two locations, one urban and the other rural. The urban site on the Indian Institute of Tropical Meteorology (IITM) campus was located about 15 km away from Pune City (18.5°N, 73.8°E, 559 m above sea level) on the outskirts in the northwest sector. Commuter vehicular traffic is the major emission source of ozone precursor gases at the IITM campus. An industrial area located about 25 km away from the IITM campus might also act as a source of precursor gases when wind flow during winter is in a northeast direction. Ozone concentration measurements were carried out from January 2001 to December 2005 at the urban site.

The rural site, Joharapur (19.3°N, 75.2°E, 474 m), is free from vehicular-traffic emission source of O_3 precursor gases. Mostly seasonal farming activities are precursor gas emission sources. To study the weekend effect in the rural region, measurements of O_3 were carried out from March 2002 to December 2005.

Measurement technique

A modified electrochemical ozone sensor was used for continuous O_3 measurements (IMD, 1999). The detection limit of the ozone instrument was 1 parts per billion by volume (ppbv), with a precision better than ± 2% (WMO, 1994). The sensor was calibrated with a UV photometric ozone analyzer (Model O342M, Environment S. A., May 2002) by running them together at an average time interval of 1 h. The correlation coefficient was 0.86.

Data

Hourly averages of O_3 concentration were computed from the continuous ozone record. The diurnal hourly average for the study period was computed from hourly averages of O_3 concentration for Monday through Friday as weekday O_3, and for Saturday through Sunday as weekend O_3. The hourly average maximum ozone concentration at noon was also computed for monthly weekend and weekday. For monthly, the seasonal mean of weekend and weekday O_3 was computed for different seasons during the study period: summer (March-May), monsoon (June-September), post-monsoon (October-November) and winter (December-February). Seasonal averages were computed from monthly averages of maximum O_3 concentration observed at noon.

RESULTS AND DISCUSSION

Ozone concentration over the Indian region depends on photochemical production of O_3 related mainly to NOx concentration. Commuter vehicle is the major source of NOx emission at the urban site, where it is assumed that weekend traffic density is lower than on weekdays. However, in spite of low weekend NOx emissions, high O_3 concentration was observed at both the Joharapur and the Pune sites. Table 1 shows that the seasonal average of maximum O_3 concentrations observed at noon (1100-1600 h) when, for the study period at both sites, O_3 concentration on weekend was greater than weekday during four seasons (summer, monsoon, post-monsoon, and winter). Weekend ozone was higher than weekday for 25 weeks (50%) and 30 weeks (60%) for the rural and urban site, respectively, and in the corresponding remaining week, weekend ozone was lower than weekday.

Table 1 shows that the higher O_3 was observed on weekend compared to weekday at both sites. The occurrence of weekend O_3 effect was determined by the differences in O_3 concentration between weekend and weekday. The criteria used were classified in three categories: a) intense weekend effect if O_3 difference is > 15 ppbv; b) moderate weekend effect if O_3 difference is 5-15 ppbv; and c) no weekend effect if O_3 difference is < 5 ppbv (Blanchard and Fairley, 2001). Using

the above criteria, it can be seen that intense weekend effect is observed in summer (> 16 ppbv difference) during the years 2003 and 2004 at the rural site, and in the winter in the urban site (34.0 ppbv difference) during 2005. Moderate weekend effect at both sites was observed mostly in winter, premonsoon, and summer for three years during 2003, 2004 and 2005. For the year, moderate weekend O_3 effect occurred for 12 weeks (25%) in the urban, and 10 weeks (20%) at the rural site. However, no weekend effect is observed in the monsoon season at either the rural or the urban site.

It is also seen from Table 1 that from 2003 to 2005 the weekend O_3 effect increased at the urban site, while no systematic increase was observed at the rural site. This indicates that weekend photochemical production of O_3 was more sensitive and more quickly disturbed at the rural site, while being less disturbed at the urban site. Apparently, weekend O_3 phenomenon depends largely on differences in NOx concentration between weekday and weekend, together with the sensitivity of VOC towards the photochemical production of O_3, which occurs quickly for some VOCs at low NOx concentrations (Qin *et al*., 2004). Qin *et al*. (2004) reported that VOC sensitivity, combined with a decrease in weekend NOx emissions, caused weekend O_3 effect. At the urban site, where weekend commuter vehicular emissions are lower, emissions consisted of about 95% nitric oxide (NO), and very low nitrogen dioxide (NO_2) and VOC concentration. Increased traffic from Monday to Friday increased NO concentrations responsible for decreased O_3 concentrations on weekdays. The major NOx emission related to commuter vehicles on weekday leading to suppressed O_3 conventions was due more to the strong NOx titration ($O_3 + NO = NO_2 + O_2$) compared to weekend. Liu *et al*. (1987) reported that the photochemical production of O_3 decreases as NOx concentration increases. On the other hand, weekend commuter vehicular traffic is less compared to weekday, which results in less NOx emission and less NOx titration. Moderate weekend NOx concentration conditions inducing faster photochemical production of O_3, and less titration of O_3 by NOx result in higher O_3 concentrations as compared to weekday. In short, production of O_3 is increase, and loss is less, which leads to elevated weekend O_3 concentration at the urban site.

At the rural site, NOx concentration due to emissions from local activities was low, and to some extent was transported from nearby developing urban areas; thus, contributing to O_3 production. While photochemical production of O_3 depends on NOx concentration in a NOx-limited environment over this region, it was observed that the above relationship is not valid in summer and winter. Production of O_3 was higher on weekend than weekday in spite of low NOx concentration. The emission of anthropogenic NOx was low, and a large amount of trees in the rural produces high levels of natural hydrocarbon (isoprene). The higher weekend O_3 concentration appears due to fast photochemical production of O_3 by isoprene at low NOx concentration. Benjamin *et al*. (1997) reported that isoprene emission increases with ambient temperature and solar radiation, resulting in highest isoprene emission at noon. The

photochemical production of O_3 by isoprene is highest at noon due large values of MIR as compared to other anthropogenic VOCs (Carter, 1994). In contrast, low weekday O_3 concentration seems to be due to increased NOx concentration, which reduces the photochemical production of O_3 by the oxidation of isoprene.

While weekend O_3 effect is significant in summer and winter, it is not observed during monsoon. Meteorological conditions were also responsible to some extent for intense weekend O_3 effect on a seasonal basis; however, it appears that differences in O_3 precursor gas concentration (NOx, VOC) are a major cause for this phenomenon of weekend O_3 effect. The results obtained in the present study indicate that higher O_3 concentration on weekend compared to weekday suggests that the photochemical production of O_3 is nonlinear over this region.

Table 1. Hourly averaged maximum ozone concentrations (ppbv) observed at noon when weekend ozone concentrations are greater than weekday concentrations during different seasons in the rural and urban site.

Year	Rural								Urban							
	Summer		Monsoon		Post-monsoon		Winter		Summer		Monsoon		Post-monsoon		Winter	
	WD	WE	WD	WE	WD	WE	WD	WE	WD	WE	WD	WE	WD	WE	WD	WE
2001	……								53.0	56.0	18.0	19.1	9.7	12.8	39.0	41.0
2002	34.4	44.3	18.1	22.1	34.0	36.8	30.3	36.0	51.2	54.2	28.8	31.2	10.5	11.5	33.5	35.2
2003	59.2	75.2	23.7	28.8	34.3	39.2	40.2	46.8	49.8	61.0	16.2	21.0	15.0	21.5	29.2	36.0
2004	37.1	53.6	19.1	28.8	30.4	35.8	35.6	42.1	45.0	59.3	20.3	25.2	24.0	30.0	47.3	61.2
2005	52.0	58.0	18.0	22.0	31.5	36.0	38.0	45.0	56.0	66.0	19.0	23.0	39.4	48.0	49.0	83.0

Ozone was not measured during 2001 at rural site. The computed values are seasonal averages of maximum O_3 observed at noon. WD = Weekday ozone concentrations, WE = Weekend ozone concentrations.

As discussed in the introduction, different hypotheses have been proposed by several researchers to explain the weekend ozone effect. As reported by these authors the environment is mostly NOx-saturated or VOC-sensitive in the mid and high latitude where the weekend O_3 effect occurs. However, in this study, the weekend ozone effect observed in the tropical India environment is NOx-limited. The weekend O_3 effect results obtained in this study are in agreement with results reported by the Qin *et al*. (2004). Their results suggest that the increase of VOC sensitivity for the photochemical production of O_3 at low NOx concentration on weekend is the cause of weekend O_3 effect phenomenon. However, long-term datasets for India are needed to support the variations observed in O_3 on weekend and weekday. Data are also needed for O_3 precursor gases of NOx and VOC in order to elaborate on the results obtained in this study.

Diurnal variation of ozone concentrations on weekday and weekend in the rural and urban site

Fig. 1 (a-d) shows hourly average of seasonal diurnal variation of weekend and weekday O_3 concentrations during the four seasons of summer, monsoon, post-monsoon, and winter at the rural site. Seasonal averages are computed from the weeks in which weekend ozone was higher than the weekday ozone. Fig. 1 shows that the highest maximum O_3 concentrations observed were about 75 ppbv on weekend and 64 ppbv on weekday at around 1600 h in the afternoon in summer (Fig. 1a). The corresponding next highest O_3 concentration of 42 ppbv and 38 ppbv was observed at around 1700 h in winter (Fig. 1d). The diurnal variation of O_3 was lowest in monsoon season on weekday (29 ppbv) and on weekend (34 ppbv) at noon, due to cloudy and rainy weather. However, O_3 concentration was higher on weekend than weekday by about 5-7 ppbv, due to less NOx titration at the rural site (Fig. 1b). During post-monsoon season, the average O_3 concentrations on weekday and weekend started to increase after monsoon season because of less cloud cover and favorable meteorological conditions for photochemical production of O_3 (Fig. 1c). The difference between weekday and weekend ozone was observed to be less; however, weekend ozone concentration was still higher than weekday. The higher O_3 concentration on weekend was maintained from morning throughout day and nighttime in all seasons. The higher O_3 on weekend due to decreased NOx emission resulted in less NOx titration of O_3. Decreased anthropogenic VOC emission appears to increase isoprene reactivity, which possesses high MIR (Carter, 1994). The photochemical production of O_3 depends on its precursor-gas concentration mainly on NOx and VOC sensitivity. The emission of isoprene from trees at the rural site was related to the ambient temperature (Benjamin *et al*., 1997), which was highest in the afternoon. Emission of NOx depends on anthropogenic activity mainly during daytime. Therefore, the O_3 peak appeared mostly in the afternoon at the rural site probably because of the availability of precursor gases (isoprene) for photochemical production of O_3 in the afternoon.

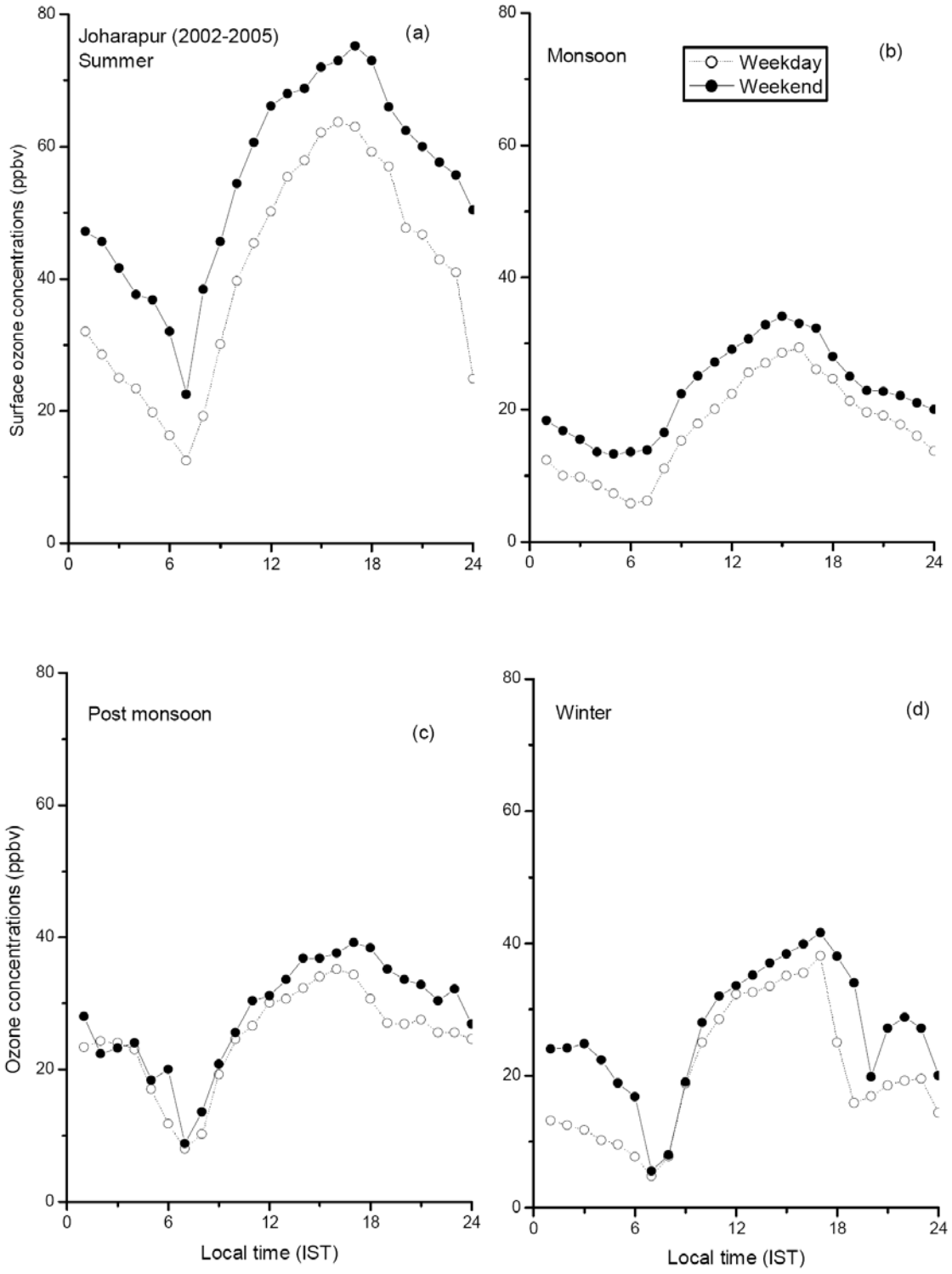

Fig. 1. Seasonal diurnal variation of ozone concentrations on weekday and weekend at the rural Joharapur measurement site, indicating that ozone is higher on weekend.

Fig. 2 (a-d) shows average seasonal diurnal variation of O_3 concentrations on weekday and weekend during four seasons from January 2001 to December 2005 over Pune, the urban site. Fig. 2a shows that the highest maximum O_3 concentration of about 80 ppbv was observed on weekend in summer, which was higher than the rural site; and 50 ppbv on weekday in summer, which was lower than the rural site in the afternoon (around 1530 h) (Fig. 2a). The winter experienced the next-highest O_3 concentration on weekday and weekend; about 66 ppbv and 58 ppbv, respectively, at 1200 h (Fig. 2d), also higher than at the rural site (Fig. 1d). The lowest O_3 concentration (< 20 ppbv) on weekend and weekday was observed in monsoon season (Fig. 2b), which was lower than at the rural site (Fig. 1b); however, it can be seen that the weekend O_3 concentration was higher than weekday concentration. The high O_3 concentration in summer was related to the active photochemical production of O_3 due to intense solar radiation and high temperature.

The average O_3 concentration in the early morning (0000-0400 h) on weekday and weekend are almost different for two sites with moderate weekend effect at the rural site in summer and winter, and no weekend effect in other seasons (Fig. 1). At the urban site, the O_3 concentration was lower (50 ppbv) on weekday than at the rural site (64 ppbv) on weekday in summer (Fig. 1a and Fig. 2a); possibly due to fresh emission of NO (from commuter vehicle) that destroyed ozone during the night. During the winter, high O_3 was observed on weekend (66 ppbv) and weekday (58 ppbv) at the urban site than the corresponding O_3 (42, 38 ppbv) at the rural site, due to trapping of O_3 near the earth's surface by temperature inversion in the atmospheric boundary layer.

Minimum O_3 concentration was observed during morning hours in all seasons at both sites. Therefore, high nighttime carryover ozone and low morning emission of NOx on weekend, as observed by Vukovich (2000a), were not observed over the present study sites, which, in this study, produced weekend O_3 effect of a minimum O_3 concentration (5-10 ppbv) attained everyday in the morning hours (0600-0700 h) in each season at both the sites.

The average O_3 concentrations in the early morning (0400-0700 h) on weekday and weekend for the rural and urban sites differ, with moderate weekend effect in summer at Joharapur and no weekend effect in summer at Pune (Fig. 1a and 2a). Hence, this study revealed that nighttime carryover O_3 is not the cause of the weekend effect at either site. The cause of weekend O_3 effect is the lack of fresh emission NO, which destroyed weekend O_3 at the urban site. Blanchard and Fairly (2001) suggested that the weekend effect is related to whether ozone formation is VOC- or NOx-sensitive, with higher weekend ozone occurring in VOC-sensitive areas, as observed in the present study at the urban site. The results obtained in this study support the hypothesis that the weekend effect is due to a combination of VOC-sensitivity and reduced NOx emission on weekends (Qin *et al*., 2004).

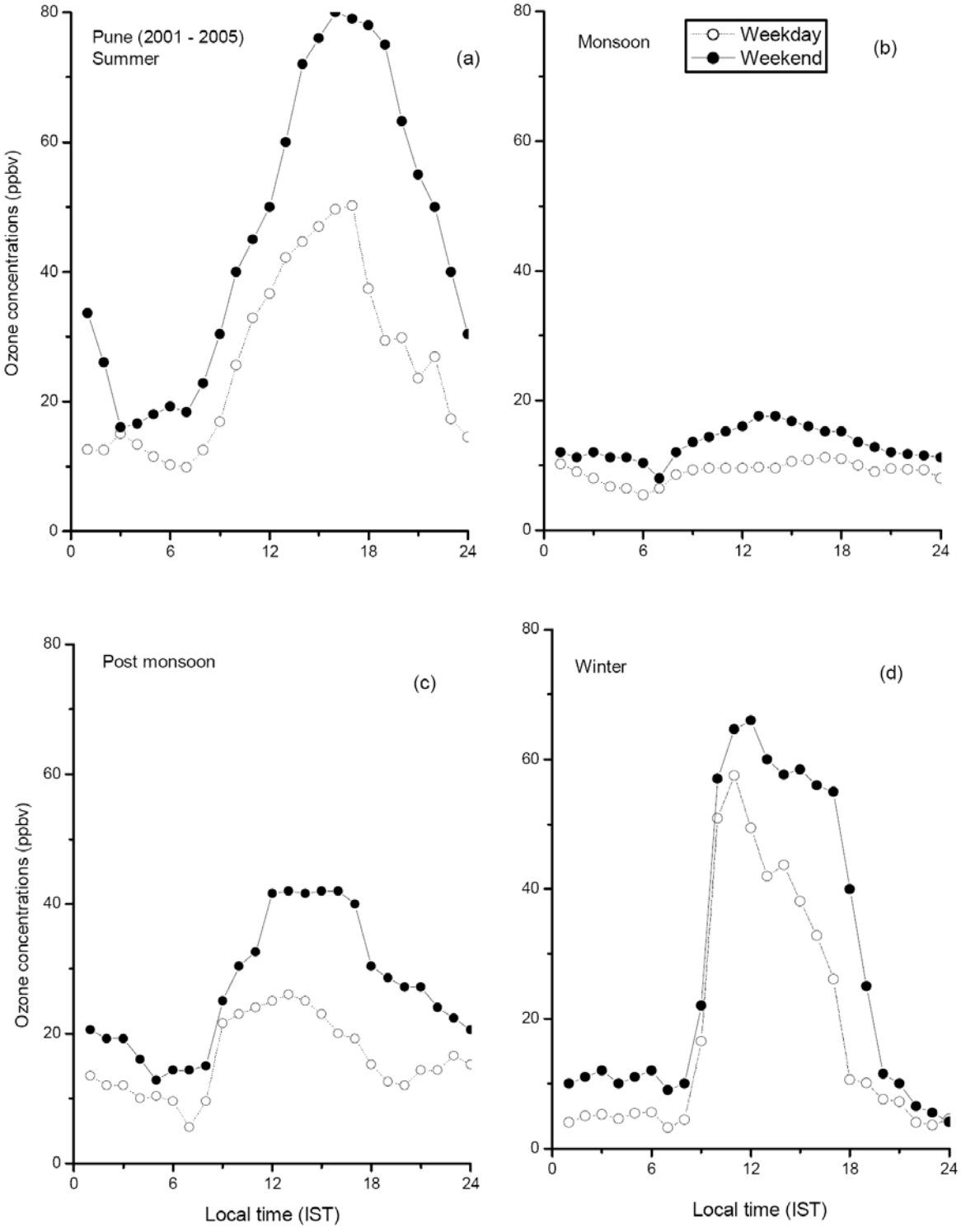

Fig. 2. Seasonal diurnal variation of ozone concentrations on weekday and weekend at the urban Pune measurement site, indicating that ozone is higher on weekend..

Comparison of weekend and weekday ozone concentration observed in the rural and urban site

Table 2. Summary of the weekend and weekday ozone concentrations differences (ppbv) observed for various ranges in rural and urban site for the period of 2001-2005.

WE and WD differences (ppbv)	Rural (%)	Urban (%)
WE>WD		
0-5	30	30
5-15	20	25
>15	00	5
b) WE<WD	50	40
c) Total	100	100

Weekend ozone concentration = WE, Weekday ozone concentration = WD

Table 2 summarizes averaged weekday and weekend ozone concentration observed for different ranges over these two sites for the study period. It can be seen that the average weekend O_3 effect observed for 25 weeks (50%) at the rural site in a single year, and 30 weeks (60%) at the urban indicates nonlinear behavior of O_3 chemistry during those weeks. In the remaining corresponding 25 weeks (50%) and 20 weeks (40%), the O_3 concentration is higher on weekday than weekend (weekend O_3 effect is not observed), indicating a linear behavior in the chemistry of O_3 production for these remaining weeks. The moderate weekend O_3 effect is observed frequently over 10 weeks (20%) and 12 weeks (25%) in rural and urban site, respectively; and the intense weekend O_3 effect (5%) is observed in urban site for only a few weeks in summer. This indicates a mixed (linear and nonlinear) chemistry behavior of O_3 production over this region. Further, it confirms that the weekend effect is not observed on every week of each month in the year; however, weekend effect is observed when production of O_3 is nonlinear. Also, the weekend effect is more pronounced during summer and winter, and not observed during the monsoon season. The spread of the weekend ozone effect (more frequent occurrences) in urban may be due to a shift in ozone formation processes from a NOx-limited to a VOC-sensitive environment.

The difference between weekend and weekday ozone concentrations in 0-5 ppbv range is observed over 17 weeks (30%) at both the sites. It is possible that, in the near future over this region, the range of O_3 (0-5 ppbv) may shift to the range of 5-15 ppbv O_3 of moderate weekend effect due to increased vehicular traffic emission, which means more weeks of weekend O_3 effect—to about 40-45 weeks (80-90%) of the year. In short, the results of this study indicate an interplay between linear and nonlinear behavior in the chemistry of O_3 production and a shifting more towards the nonlinear side in the urban site, leading to increased weekend effect over this region in the future. Data obtained in this study are needed for comparing with O_3 variation observed over this region during the presented study period. Long-term data analysis of O_3 and its

precursor gases, as well as modeling studies, are required for confirmation of results obtained in this study, as well.

CONCLUSIONS

The following conclusions may be drawn from the presented study results. Ozone concentration is higher on weekend over tropical rural and urban sites in India, where ozone production processes are NOx-limited. Moderate to intense weekend ozone effect is observed in summer and winter at both sites. The possible cause of weekend ozone effect is related to variations in VOC sensitivity, and to reductions in NOx concentration (Qin *et al*., 2004). The weekend ozone effect is more pronounced at the urban site as compared to rural, which indicates that the urban environment is shifting towards VOC-limited conditions for ozone production in the growing cities. The interplay between linear and nonlinear (mixed) behavior in the chemistry of O_3 production and a shifting towards the nonlinear side suggest near-future increases in weekend effect over this region.

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