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Surface ozone variability over western Maharashtra, India

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ABSTRACT

We present the simultaneous field measurements of surface ozone (O_3) made at the five different sites of western Maharashtra, India for the period between 2001 and 2005. Seasonal variation in O_3 shows a pronounced maximum concentration about 40–50 ppbv in the summer and winter season in the urban site and similar concentration of O_3 is also observed in the rural site despite less emission of precursor gases. The increase in O_3 concentration is observed in the sugar factory premises during sugarcane crushing period. Diurnal patterns in O_3 do not show daytime in situ photochemical buildup at high altitude mountain site. The higher O_3 concentration is observed in the morning hours near to the dam than at urban and rural sites. These variations in O_3 indicate that the local pollutants are major contributors to the O_3 concentrations at the urban and rural sites, while regional transport plays a role at high altitude mountains site. Model simulations using a Eulerian photochemical model have also been carried out with the available data. The comparison of model results with observation shows that a diurnal and seasonal pattern is in good agreement.

1. Introduction

Ozone (O_3), one of the key trace gases in the atmosphere, is the most abundant tropospheric oxidant. The human activity (e.g. combustion which leads to the emission of nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOC), a major precursor of O_3) are responsible to increase the concentration of O_3 at the surface of the earth. The residence time (life cycle) of O_3 in the lower troposphere varies according to season and altitudes between a few days (5–8) at the ground level and a few weeks (3–15) in the free troposphere. The high O_3 concentrations and their long persistence times have now become a new and frightening aspect of life on our planet. Surface O_3 is produced as a by-product of the oxidation of carbon compounds (VOC, carbon monoxide (CO) and methane (CH_4)) in the presence of NO_x by photochemistry; and O_3 formation are influenced by the sunlight intensity [1]. Photochemical production of O_3 is dependant on its precursor gases concentration (NO_x, VOC, CO, CH_4) and prevailing atmospheric conditions. Liu et al. [2] reported that the production processes of O_3 are highly complex and non-linear in nature. A recent review by Vingarzan [3] revealed that ozone concentrations are increasing at the rate of 0.5–2% per year over the Northern Hemisphere due to increase in human activities.

Surface O_3 is a highly oxidizing agent; its high reactivity causes detrimental effects on all living organisms and materials. Humans are likely to be affected at O_3 concentrations above 80 parts per billion by volume (ppbv). World Health Organization guideline value for O_3 is 77–102 ppbv averaged over 1 h. The U.S. health related National Ambient Air Quality Standard for O_3, based on a single day, maximum hourly exposure, is 120 ppbv for 1 h, not to be exceeded more than once per year [1]. However, at low levels of O_3 (<120 ppbv) can also produce significant changes in respiratory function in humans has been well established and it exposure can cause premature aging of the lungs [4]. Mulholland et al. [5] reported that O_3 can increases 4% in pediatric asthma rate per 20 ppbv increase in surface O_3 concentration. Further, recent studies have shown that the number of excess O_3 related deaths of around 600–2045 during the summer period June to August 2003 in the Netherlands and in the UK compared to an 'average' summer [6,7].

Being phytotoxic in nature, surface O_3 concentration greater than 40 ppbv in the surface level can affects the agricultural crops yield and also the biomass production, vitality, and stress tolerance of the forest trees [8]. Chameides et al. [9] and Feng et al. [10] have showed the decrease in the yield of crop by 10–15% due to increases in surface O_3 concentration (>60 ppbv) at the ground level in China. The surface O_3 is also responsible for the present rapid forest decline and reduces the lifespan of various materials like rubber, concrete building, painting, etc. [11]. Further, O_3 is a powerful greenhouse gas as it absorbs the radiation at 9.6 μm wave-

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length emitted by earth's surface. Hence, it acts as the third most important greenhouse gas after carbon dioxide (CO_2) and CH_4 and contributes roughly 0.35 W/m^2 (about 8–15%) to the total radiative forcing [12]. Rapidly developing countries in the tropics and subtropics, the regions (particularly India and China in Asia) of very limited measurements of surface O_3, realized the importance of the studies on surface O_3.

A few observational studies on surface O_3 are available over the Indian region. Khemani et al. [13] reported high surface O_3 concentrations around 38 ppbv during summer season in March over semi urban site, Pune. Lal et al. [14] and Sahu and Lal [15] have shown that surface O_3 (here after O_3) concentration was in the range of 30–43 ppbv at the urban site of Ahmedabad (23°N, 72.6°E, 49 m asl) during the winter and a similar concentration of O_3 at the rural site of Gadanki (13.5°N, 79.2°E, 375 m asl) during the summer season [16]. Recently, Beig et al. [17] reported that average high O_3 concentration of 55 ppbv in February during the winter at semi urban site of Pune was attributed to the regional transport from the sugar factories/industries. These previous observation-based studies in India have attempted to determine the behavior of O_3 were aimed for either in urban or rural environmental condition but not for both. We change the focus and present a systematic O_3 behavior in both urban and rural environment simultaneously to determine the relative importance of chemistry and transport.

In this study, simultaneous continuous measurements of O_3 were made at five different sites over western Maharashtra, India along with different environmental conditions. To the best of our knowledge, combined simultaneous measurements of O_3 at both urban and rural sites over the Indian region prior to this study have not been made earlier. Therefore, these measurements will help to understand the various processes including regional transport and in situ photochemical production of O_3 especially over rural sites in Indian tropical region. It is also stressed that local emissions of precursor gases and seasonal cycle of meteorological parameters can play a predominant role to influence the photochemical regimes of O_3. Results of O_3 measurements are discussed in the light of available meteorological parameters and chemical precursor gases NO_2 and CO estimated from satellite plots.

2. Observational sites and instrumentation for ozone measurements

2.1. Observation sites and general meteorology

Five different sites are selected with different atmospheric conditions to explore the diurnal and seasonal pattern of O_3 concentrations over western Maharashtra, India in the present study (Fig. 1). Continuous measurements of O_3 were made from January 2001 to December 2005 at Pune in the Indian Institute of Tropical Meteorology (IITM) campus, a representative of semi urban site. Second site was rural; Joharapur, O_3 was measured from January 2002 to December 2005. Third site was premises of Sugar factory, Bhenda, O_3 was measured for one complete crushing period (before, during and after the crushing of sugarcane) for the period from November 2004 to March 2005; and fourth site, remote rural near to the dam, Mulanagar for the period from March 2005 to June 2005 which is surrounded by high mountain hills on both sides and far away from the human activities (similar to forest environmental condition). The measurements of O_3 have also been made from November 9 to 17, 2005 at high altitude mountain rural site (fifth site), Mahabaleshwar. In this way, these five different sites signify large variations in topographical conditions ranging from remote dam surrounded by hills to high altitude mountains and from urban to rural and sugar factory. Table 1 shows the location, classification and O_3 measurements period of the each site.

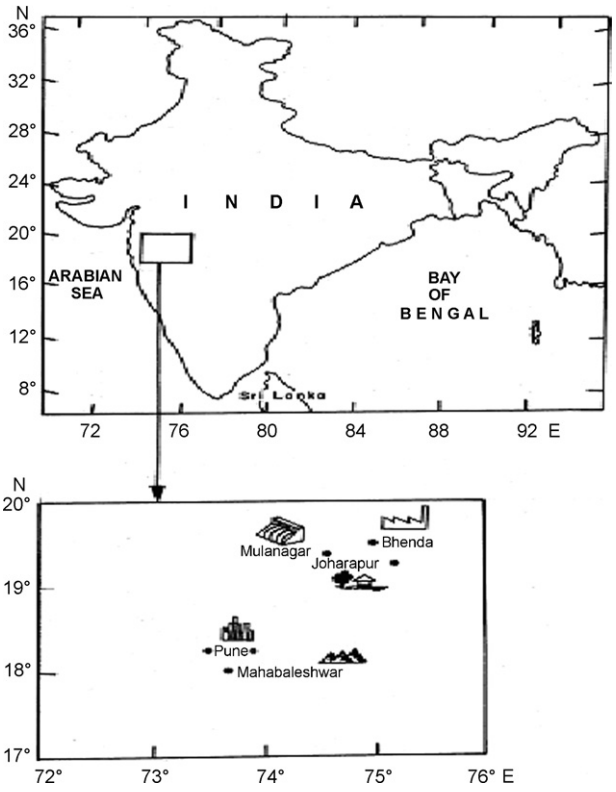

Fig. 1. Location map of the India shows five different observation sites of surface ozone (urban, rural, mountain, sugar factory and dam) over western Maharashtra, India.

Table 2 presents the average seasonal cycle (average monthly) of meteorological parameters such as maximum, minimum and average temperature, incoming solar radiation, relative humidity (RH), rainfall (RF), cloud cover (CC) and wind speed (WS) and direction reported for 2001–2005 by Indian Meteorological Department (IMD) at Pune [18]. The seasonal cycle of meteorological parameters is related with the seasonal cycle of O_3 measured over the study region. The unique feature of the present study region is the southwest monsoon wind from Arabian Sea which brings rainfall activity over Indian region from June to September that amounting to 80% of the total annual normal rainfall, seems to play an important role in seasonal as well as in diurnal variability of O_3. The annual rainfall 57, 42, 45.9, 91.3 and 133.9 cm was recorded for the year 2001, 2002, 2003, 2004 and 2005, respectively (annual normal rainfall: 67 cm) over Pune. Southwest wind brings monsoon and clean air (in particular over the study region) to India by the northward propagation of Inter Tropical Conversion Zone (ITCZ). The weather during post-monsoon season from October to November is calm and some times scattered rainfalls occur. Fair weather conditions prevail during the winter season from December to February with calm wind speed with northeasterly direction, clear sky and moderate relative humidity of 20–70%. Northeasterly wind brings the polluted air over the study region. The summer (premonsoon) season period from March to May experiences hot weather due to intense incoming solar radiation, which accelerates the photochemistry of O_3 production. However, sometimes pre-monsoon shower disturbs the photochemical production of O_3 in some years. The surface air temperature reaches around 43 °C during day and 25 °C in the night over the study region.

Table 1
Details of the location, description and period of ozone measurements of the site over western Maharashtra, India

Station	Location	Site classification	Monitoring period
Pune	18.5°N, 73.8°E, 559 m	Semi urban	2001–2005
Joharapur	19.3°N, 75.2°E, 474 m	Rural	2002–2005
Bhenda	19.5°N, 75°E, 480 m	Sugar industries	November 2004–March 2005
Mulanagar	19.4°N, 74.6°E, 657 m	Dam, remote rural	March 2005–June 2005
Mahabaleshwar	18°N, 73.7°E, 1382 m	High mountain	November 2005

Table 2
Average monthly meteorological condition observed for 2001–2005 over the study region at Pune

	Temperature (°C)			Radiation (W m^{-2})	RH (%)	RF (mm)	CC (%)	Wind	
	Maximum	Minimum	Average					Speed (m/s)	Direction
January	33.4	8.2	20.6	682	56	0	36	0.4	NNE
February	36.8	7.3	22.6	892	39	0	22	2	NNW
March	40.1	11.7	25.9	935	32	0	29	3	NNW
April	39.5	14.1	29.2	955	40	25	38	3	NNW
May	41.3	19.4	30.3	1012	58	30	45	4	WNW
June	36.4	21.1	26.9	860	74	120	82	4	WSW
July	31.5	21	25.3	576	80	225	83	3	SW
August	29.2	20.6	24.3	771	83	164	85	3	S
September	32.2	15.9	26.5	785	81	86	70	3	NW
October	32.8	12.7	25.7	950	67	60	67	1	N
November	32.6	10.5	24.1	812	61	30	35	1	NNE
December	32.1	8.1	22.4	805	60	0	42	0.5	N

Average monthly concentration of NO_2 and CO, a major precursor of gases of O_3 formation, was estimated from the satellite plots (website: http://www.temis.nl/airpollution/no2col/SCIAMACHY Version 1.1 for NO_2 and website: http://mopitt.eos.ucar.edu/mopitt/data/plots/MOPITT for CO at 850 hPa level) over Pune for 2003–2007 is shown in Table 3. The estimated seasonal cycle of NO_2 and CO was compared with the seasonal cycle of NO_x and CO measured at ground level for 2003–2004 [17]. It is seen from Table 3 that there is a quantitative agreement with the estimated NO_2 and CO from satellite plots and measured NO_x and CO concentration of seasonal cycle. Estimated low concentrations of NO_2 and CO during monsoon season months well agree quantitatively with the measured NO_x and CO concentration. Similarly, estimated high concentration of NO_2 and CO during winter and summer months was also in good quantitative agreement with the measurements. Measurements of NO_x and CO are not made in the present study; hence the satellite plots are utilized to understand the seasonal cycle of NO_2 and CO concentration quantitatively but not qualitatively over the study region. These plots are quite consistent with the location of human activity and related emissions. The estimated seasonal cycle of NO_2 and CO concentration is related with the seasonal cycle of O_3 measured. The chemistry of the atmosphere is dominated by solar radiation which induces a photolysis of certain molecules into reactive atoms or free radicals [1]. The photolysis of ozone:

$$O_3 + h\upsilon \rightarrow O_2 + O(^1D), \quad \lambda \leq 315\,\text{nm}$$

This key photolysis leads to the formation of hydroxyl radical (OH) involved in the oxidative removal/decomposition of most trace gases in the troposphere emitted by the human activities. Hence, OH radical term as a detergent of the lower atmosphere/troposphere which removes the almost all pollutants. The photolysis of nitrogen dioxide:

$$NO_2 + h\upsilon \rightarrow NO + O(^3P), \quad 290 \leq \lambda \leq 400\,\text{nm}$$

This reaction contributes to the chemical formation of O_3, which is the only source of photochemical ozone in the troposphere indicates that in the absence of photolysis of NO_2 there is no ozone formation [1]. Further, it infers that combustion processes

Table 3
Comparison of average monthly concentration of nitrogen dioxide (NO_2) and carbon monoxide (CO) estimated from satellite plot over the study region and with measurements available of NO_x and CO at Pune

	Estimated from Satellite[a]		Ground level measurements[b]	
	NO_2	CO	NO_x	CO
January	3.3 (0.189)	168	16.1	750
February	2.8 (0.160)	143	13.5	–
March	3 (0.171)	182	11.2	600
April	3.5 (0.200)	175	8.5	400
May	2.8 (0.160)	136	6.8	350
June	3 (0.171)	98	3.6	300
July	2 (0.114)	63	2.8	300
August	1.5 (0.085)	69	3.2	300
September	1.9 (0.108)	99	4.1	350
October	3 (0.171)	126	8.6	400
November	3.2 (0.183)	170	15.5	700
December	2.7 (0.154)	165	20.7	800

[a] SCIAMACHY (2002–2007) (NO_2 density [10^{15} mol/cm^2]), NO_2 values in ppbv are shown in parentheses. MOPITT (2001–2007) (CO (ppbv)).
[b] June 2003–May 2004, NO_x and CO in ppbv over Pune [17].

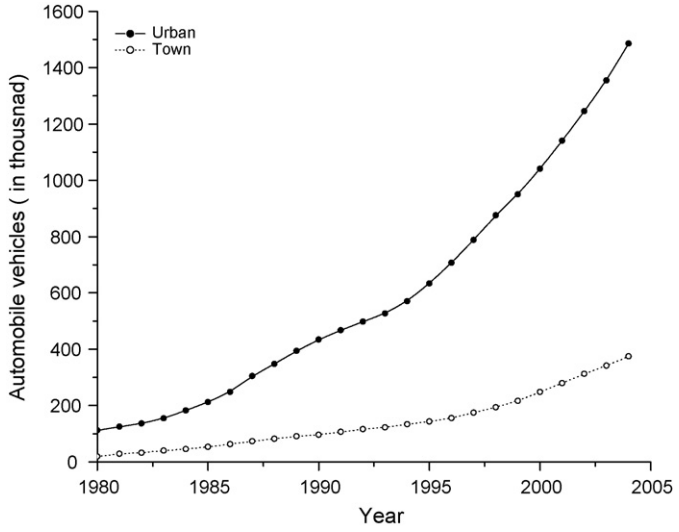

Fig. 2. Growth of the registered automobile vehicles in the urban and in town for 1980–2004 in the study region.

by human activities which emit the NO_x are mainly responsible for increasing of O_3 concentration at the ground level.

Rapid industrialization and urbanization are causing serious air pollution problems in India. Sources of air pollution include vehicular emissions and power plants and other industries growth. The air pollutants like O_3 are also expected to rise rapidly in urban, as well as in the rural areas due to transport of precursor gases from cities. Recent report on Motor Transport Statistics for Maharashtra State, India [19] shows the rate of increase of transport vehicle is about 12% per year in the urban (Pune) and similar in the town (Ahmednagar (19.1°N, 74.8°E, 657 m asl) about 100 km of northeast from Pune) for 1980–2004 (Fig. 2). The increase in vehicular traffic density from more than last two and half decades is related with the increase of daytime maximum O_3 concentration (from about 23–60 ppbv) and average O_3 over this region. Garg et al. [20] reported the major emission of NO_x about 32% is from vehicular transport and rural biomass burning contributes 18% of the total emission (3.46 Tg) in 1995 over the Indian region which is effective sources of O_3 precursor gases. Asian emission inventory in 2000 by Streets et al. [21] show the transport sector contribution has increased from 32% to 34% to total NO_x emissions (4.59 Tg) and is growing at an annual rate of about 6.5% which is higher by 1% than the earlier estimate [20] in India.

2.2. Ozone measurements technique

The electrochemical O_3 sensors have been used for simultaneous continuous measurements of O_3 at all the five sites [22]. The detection limit of the O_3 instrument is 1 ppbv and the precision better than ±2% [23]. The ozone sensor was calibrated with the ultraviolet (UV) photometric ozone analyzer (Model $O_3$42 M, Environment S. A., May 2002) by running them together with averaging time interval of 1 h, and correlation coefficient is found to be 0.86. All data analyses in this paper are based upon the hourly averaged, Indian Standard Time (IST). IST is 5.5 h plus Greenwich Mean Time. In addition, the continuous air temperature, relative humidity and incoming solar radiation are also measured at Pune, Joharapur and Mahabaleshwar. The cloud cover, air temperature, rainfall, relative humidity, wind speed and direction data are used to explore atmospheric conditions over the study region for 2001–2005 from IMD [18].

2.3. Photochemical model

To study the ozone behavior and its precursor gases over the study area, we use a Eulerian photochemical model to simulate diurnal and monthly O_3 concentration, using Euler's numerical techniques assuming quasi steady state approximation (QSSA) and simple chemistry and mass balance of O_3. Details of model formulation and simulation are given elsewhere [24]. The model requires hourly input data of NO, NO_2, J_{NO_2} (photolysis rate of NO_2 related to the intensity of solar radiation) and temperature for computation of chemical rate constant (k) of the reaction ($O_3 + NO \rightarrow O_2 + NO_2$). Simulation of O_3 concentration was carried out at Pune latitude and compared with measured O_3 concentration. These inputs are computed using required available NO_x, temperature and radiation data for 2003–2004 at Pune [17].

3. Results and discussion

3.1. Diurnal variations in ozone at urban and rural sites

Average diurnal variations of ozone for different months from January to December for 2001–2005 at urban site Pune are shown in Fig. 3. Vertical bars show single standard deviation. Measurements show that daytime maximum O_3 concentration (10–60 ppbv) due to the in situ photochemical production of O_3. Ozone concentrations are observed to be low during nighttime, as there is no photochemical production of O_3. The minimum O_3 concentrations (3–17 ppbv) are observed during early morning hours, near the sunrise time. Minimum concentration of O_3 during early morning hours is due to the loss of O_3 by NO:

$$O_3 + NO \rightarrow O_2 + NO_2$$

NO concentration is higher in the morning due to the lowest temperature at the sunrise.

In the seasonal cycle of O_3, highest O_3 concentration (40–50 ppbv) is observed during summer in the month of March or April due to the high concentration of precursor gases (NO_2 and CO) and intense solar radiation which increases the rate of chemical reaction of O_3 production at the higher temperature (Tables 2 and 3). On many occasions hourly average O_3 concentrations exceeds 80 ppbv (up to 90 ppbv) at noon in summer season were also observed. Similarly, higher O_3 is observed in December and January during the winter season due to low temperature and less boundary layer height which accumulate the O_3 at the ground level. During monsoon months (June–September) lowest O_3 concentration 4–7 ppbv was observed due to clean and moist air from the Arabian Sea, diffused incoming solar radiation and high cloud cover. Rainfall wash out the active radicals involved in the O_3 formation processes and results in the diurnal variation of O_3 nearly flat in the monsoon months. Accumulation of active nitrogen species (NO_y) especially PAN and NMHCs due to reduced temperature and low concentration of OH radicals in winter would continue till early summer [1]. Subsequent warming at the onset of summer causes pulsed input of NO_x at the ground level. This abrupt supply of NO_x and NMHCs and increased incoming solar radiation appears to be the cause of buildup of photochemical O_3 results in summer peak of ground level O_3.

Similarly, Fig. 4 shows the monthly mean diurnal variations of O_3 concentrations for 2002–2005 at a rural site, Joharapur. The highest O_3 concentration (35–45 ppbv) was observed during the summer months, however diurnal amplitude (maximum O_3 minus minimum O_3) is smaller as compared to the urban site at Pune due to the low precursor gases concentration in the rural site. The O_3 con-

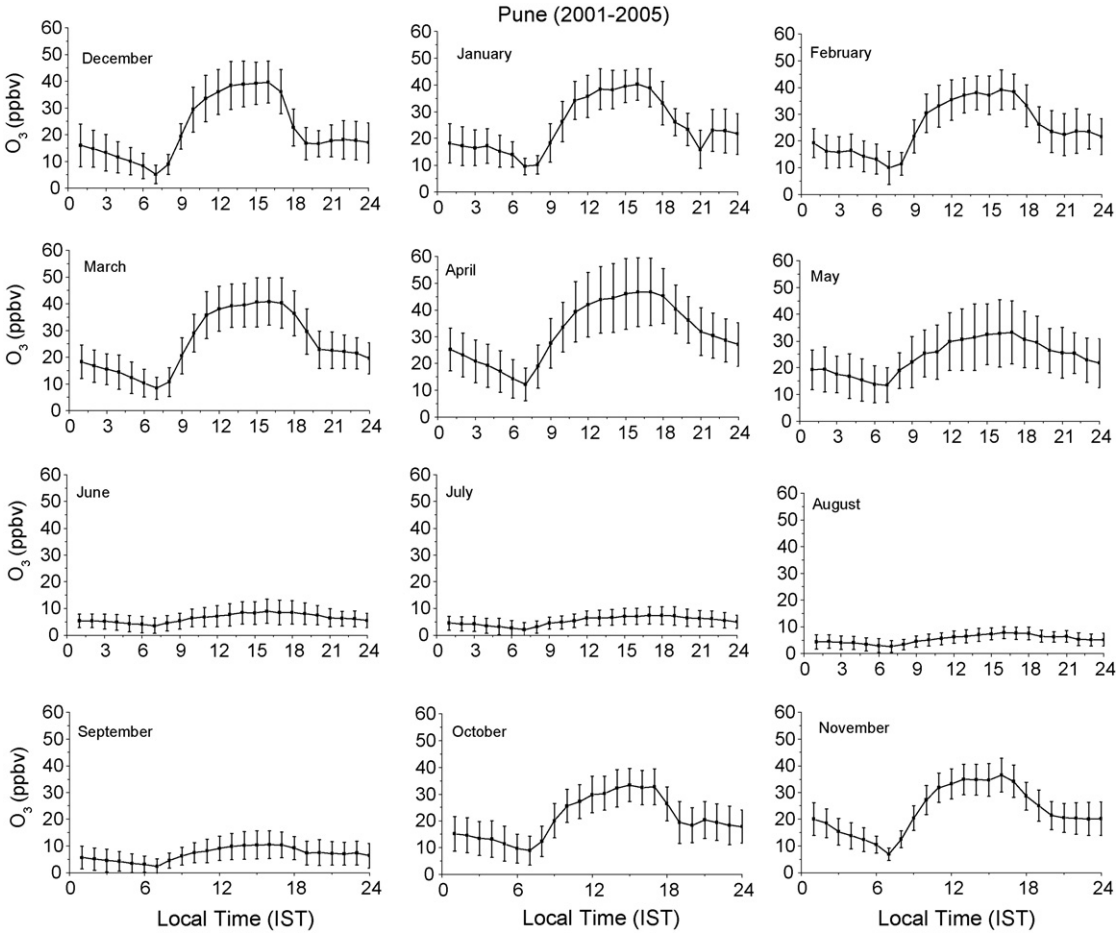

Fig. 3. Average diurnal variations of ozone concentrations in different months for 2001–2005 measured at semi urban site, Pune. Vertical bars are 1σS.D.

centration reached up to 75 ppbv at noon during summer season in April on few occasions. Comparison of Figs. 3 and 4 shows that the variations in the diurnal amplitude is higher in all months at urban site (5–35) than at the rural site (10–33). Further, it is important to note that during the monsoon months (June–September) relatively higher ozone concentration (10–15 ppbv) was observed at rural site than at urban site (Fig. 3) due to the inefficient O_3 destruction mechanism owing to the less emission of NO_x in the rural areas.

3.2. Changes in diurnal patterns of O_3 at five different sites

The variation of O_3 within a day may be helpful in delineating the processes responsible for O_3 formation or loss at a particular site. Fig. 5a–e show the diurnal variation of O_3 at five different sites. The maximum photochemical buildup (peak) of O_3 was observed during daytime usually at noon at Pune, Joharapur, Mulanagar and Bhenda site (Fig. 5a–d) due to the photochemical buildup of O_3 by photolysis of NO_2. Similarly, the minimum of O_3 was observed at all four sites during nighttime as there is a loss of O_3 by nitric oxide (NO) (titration). In addition to this, during nighttime, the photochemical production ceases. In the diurnal cycle of O_3, the minimum concentration was observed during early morning hours near the sunrise time. The diurnal magnitude of O_3 was nearly similar in the urban and in rural sites, which indicates that precursor gases load has increased in the rural site due to transport of precursor gases from nearby cities. It is noted that the time of occurrence of pronounced peak of O_3 was varied from season to season in the urban site. In the urban site, the peak of O_3 33.1 ± 5.5 ppbv (the average concentration of O_3 with 1σ standard deviation) concentrations was observed before noon at around 11:30 h local time in winter because of fast photochemical production by freshly emitted precursor (NO) from the vehicular traffic in the morning hours [25], while rapid loss of O_3 also noticed in the afternoon by same NO because of dominant titration (Fig. 5a) [14,17]. Similarly, Tiwari and Peshin [26] reported the forenoon (1000–1200 h) sharp peak (narrower) in O_3 concentration during the winter in January at Pune, which is similar to the present study. However, this forenoon pronounced broader peak of O_3 is shifted to afternoon in the summer. On the other hand, in the rural site peak O_3 29.7 ± 5.7 ppbv occurred in the afternoon around (14:00–16:00 h) local time in all seasons, probably, due to the late emission of natural precursor gases like isoprene, hydrocarbons from crops and trees which has high potential for O_3 formation is related to ambient air temperature which is generally observed in the afternoon [27] and relatively very less O_3 loss by NO owing to the negligible vehicular traffic emissions in the evening (Fig. 5b). The maximum of O_3 concentration 33.8 ± 4.5 ppbv was observed during daytime near to the dam, similar to the urban site Pune and rural site Joharapur. On the contrary, the morning hour's concentration of O_3 around 18.5 ± 5.2 ppbv was observed to be highest near to the dam as compared to corresponding concentration of O_3 in the urban and rural sites (Fig. 5a–c). It appears from Fig. 5c that the loss of O_3 during nighttime was

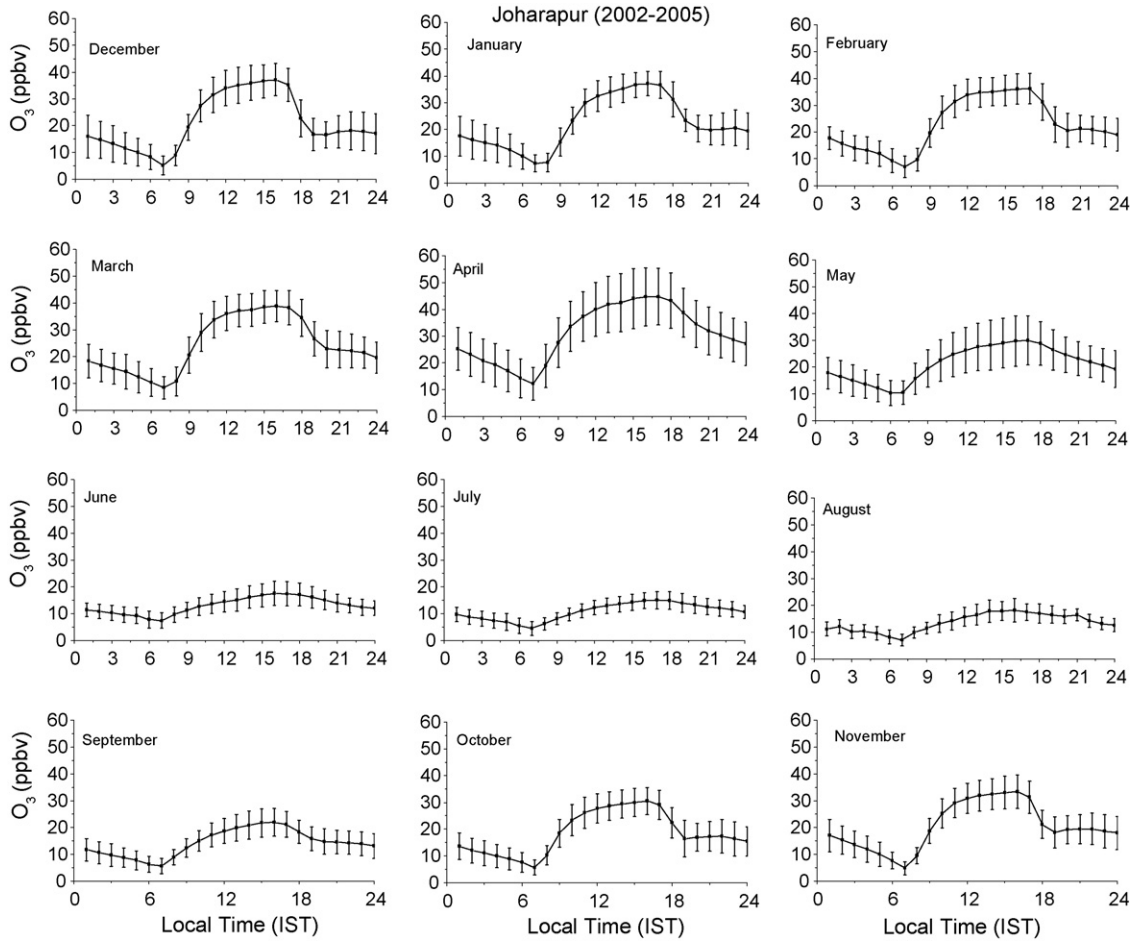

Fig. 4. Same as Fig. 3 but for measured at Joharapur rural site for 2002–2005.

slower near to the dam results in higher concentration of O_3 in the morning.

In the sugar factory premises, higher O_3 concentrations are observed during the working days of sugar factory (sugarcane crushing period) than the non-working days of sugar factory indicate that higher emission of precursor gases during working days, in particular of NO_x and hydrocarbons (Fig. 5d). Further explanation for higher O_3 during crushing of sugar factory is discussed later in Fig. 8b.

On the contrary, at the high altitude mountain site, Mahabaleshwar, minimum of O_3 32.07 ± 4.24 ppbv was observed during the daytime at noon around 13:00 h and maximum of O_3 40.2 ± 5.5 ppbv during the nighttime in the early morning hours around (03:00–04:00 h) local time (Fig. 5e). The low O_3 concentration in the daytime indicates that in situ photochemical build-up is not dominant. Hence, pronounced peak in O_3 at daytime (as observed at the other sites, Fig. 5a–d) is not observed. It appears that NO concentration seems to be below the threshold limit of O_3 formation (50 parts per trillion by volume (pptv)), which was not allowing to buildup of O_3 concentration during daytime by photochemical production. On the contrary, under this condition odd hydrogen radical's (which generate O_3) photochemistry:

$$O_3 + HO_2 \rightarrow 2O_2 + OH$$

produces net loss for O_3 during the daytime. Thus, diurnal cycle of O_3 at mountain site was completely different from the other four sites. The maximum of O_3 was observed during the nighttime seems to be due to the regional transport of O_3 from nearby cites. Lifetime of O_3 also increases with the height at the high altitude mountain site. The stratospheric intrusion/input of ozone into the troposphere at the ground level is impossible over the latitude of Mahabaleshwar (18°N), which is in the tropical region [28] indicate that diurnal O_3 variability is mainly due to transport of O_3 from nearby cities and destruction of O_3 during daytime. Significant differences were found in the diurnal patterns at the five different sites over this region. It appears that a diurnal pattern of O_3 concentrations is a function of site. The hourly averaged O_3 concentration in the daytime at all rural sites was higher than permissible limit of 40 ppbv for the crop, suggests that winter crops yields may affect as per the AOT40 concept over this region due to the increasing of O_3 pollution [8–10,29].

Fig. 6a–d shows the comparison of average diurnal variations of O_3 concentrations with diurnal variations of incoming solar radiation and air temperature measured during November 2005 at the urban, rural and mountain site. It is seen from Fig. 6a that O_3 increases with increase of incoming solar radiation over urban site. The maximum of O_3 48 ± 2.8 ppbv was observed in the daytime at around 11:00 h and minimum 5 ppbv in the morning at 07:00 h, and corresponding maximum incoming solar radiation $896.43 \pm 120.63\ W\ m^{-2}$ at 12:30 h at urban site. On the contrary, O_3 decreases with increase of incoming solar radiation at mountain site Mahabaleshwar Fig. 6b. The minimum of O_3 concentration around 32 ppbv was observed during the daytime at

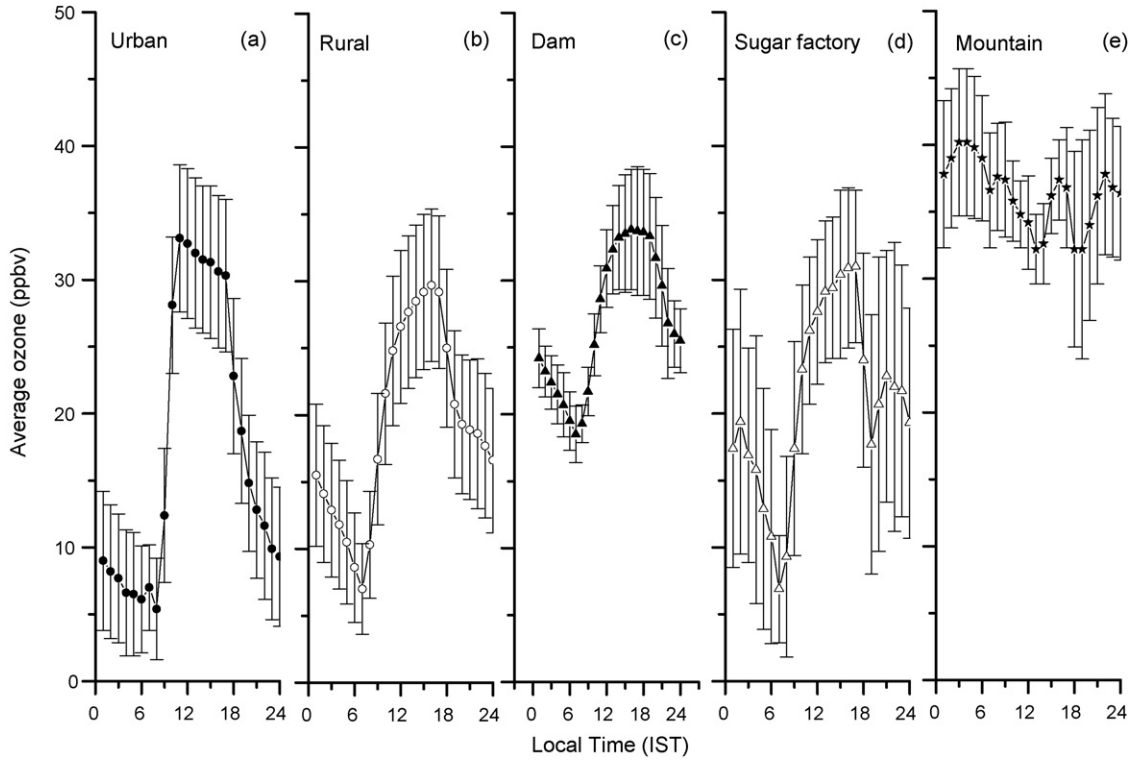

Fig. 5. Comparison of diurnal variability of surface ozone concentrations observed at (a) urban, (b) rural, (c) dam, (d) sugar factory and (e) mountain site.

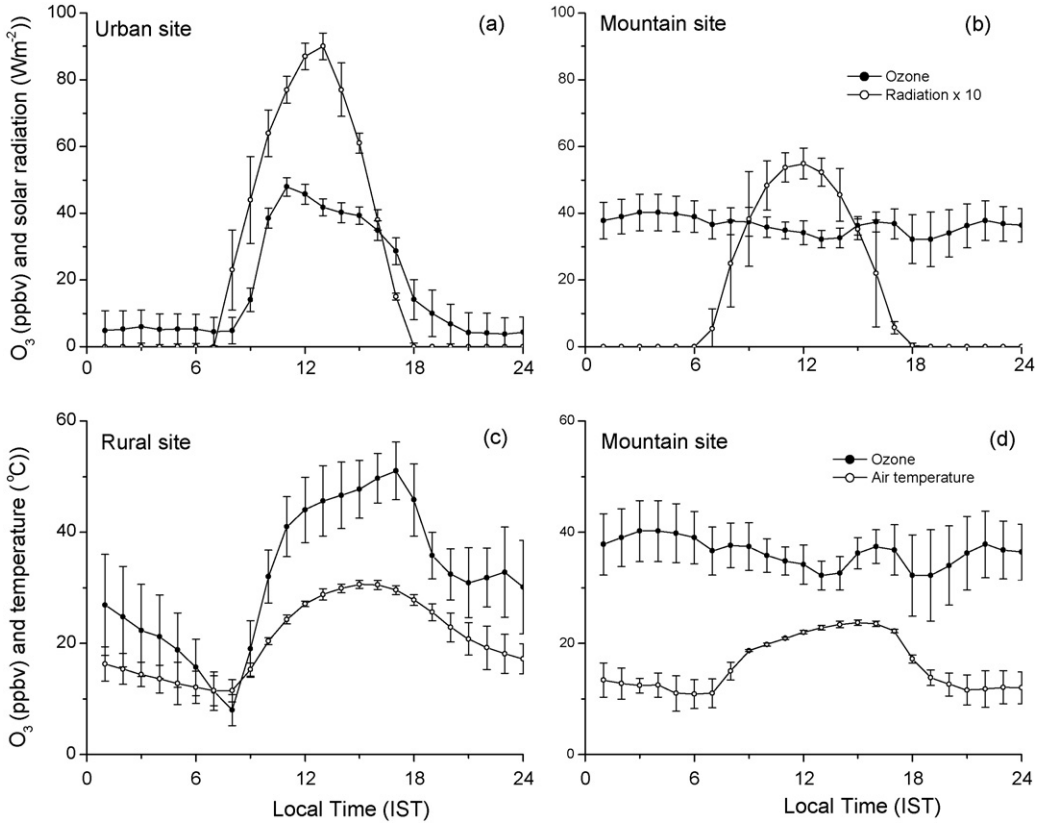

Fig. 6. Variation of average diurnal ozone concentrations with incoming solar radiation observed at urban (a) and mountain site (b) and with temperature at rural (c) and mountain site (d). Vertical bars are 1σS.D.

13:00 h. Corresponding maximum solar radiation was observed to be $549.27 \pm 65.76\ W\ m^{-2}$ at 12:00 h during daytime. The maximum of O_3 40.2 ± 5.5 ppbv observed during nighttime at about 04:00 h because of transport of O_3 from near by cities. The loss of O_3 by NO is less and lifetime of O_3 increases with decease of temperature during night at high altitude mountain site.

Fig. 6c and d shows the comparison of average diurnal variations of O_3 with diurnal variations of temperature measured at rural and mountain site. The O_3 concentration increases with increase of air temperature during daytime in the rural site (Fig. 6c). On the contrary, O_3 decreases with increase of temperature in the daytime at the mountain site (Fig. 6d). This indicates that diurnal patterns of O_3 were not related to the diurnal patterns of air temperature at high altitude mountain site, whereas it was closely related with diurnal patterns of air temperature at rural sites. It appears that O_3 concentration was not buildup by photochemical production of O_3 during daytime at high altitude mountain site. On the contrary, the mountain site experiences constant higher O_3 level in the range of 30–40 ppbv during the day and nighttime as compared to the urban and rural sites O_3 of 5–50 ppbv. Thus, there is a significant temporal and spatial variation in the O_3 concentrations due to the differences in meteorological and topographical conditions. In the urban and in rural sites daytime maximum of O_3 due to the photochemical buildup, whereas maximum of O_3 during nighttime at high altitude mountain site is attributed to the transport of O_3 from nearby cites.

Fig. 7 shows the comparison of diurnal variation of O_3 observed at Mahabaleshwar with the other mountain sites in India, Mt. Abu (24.6°N, 72.7°E) [30] and Cerro Tololo, Chile (30°S, 70°W) [31]. Vertical bars are 1 sigma standard deviation. Fig. 7 shows that O_3 measured at Mahabaleshwar are consistent with the earlier measurements reported at Mt. Abu and at Cerro Tololo. Such type of diurnal patterns in O_3 is generally observed at clean or high altitudes sites. Naja et al. [30] reported average nitric oxide (NO) concentration around 40 pptv at Mt. Abu, which is less than the threshold limit for O_3 formation. It is seen from Fig. 7 that O_3 concentration was observed to be lower in the daytime as compared to the nighttime at all three mountainous sites are due to the lack of photochemical buildup of O_3 in the daytime, and less titration of O_3 during the nighttime by NO. The diurnal variation at these three

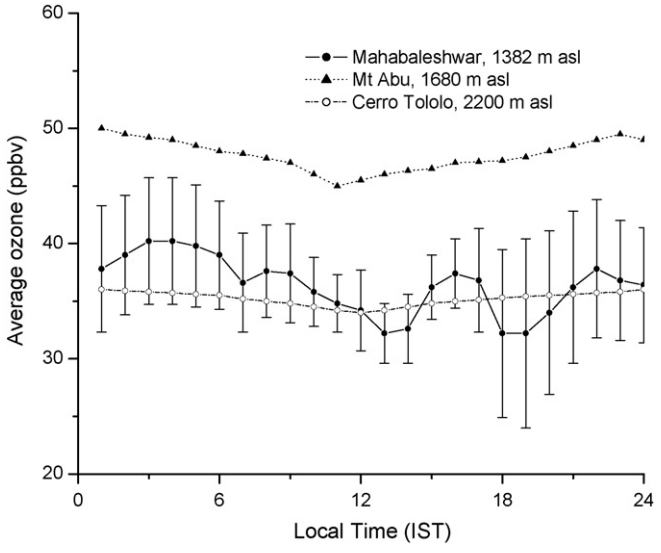

Fig. 7. Comparison of average diurnal ozone concentrations observed at mountain site, Mahabaleshwar with those of other mountain sites at Mt. Abu and Cerro Tololo, Chile. Vertical bars are 1σS.D.

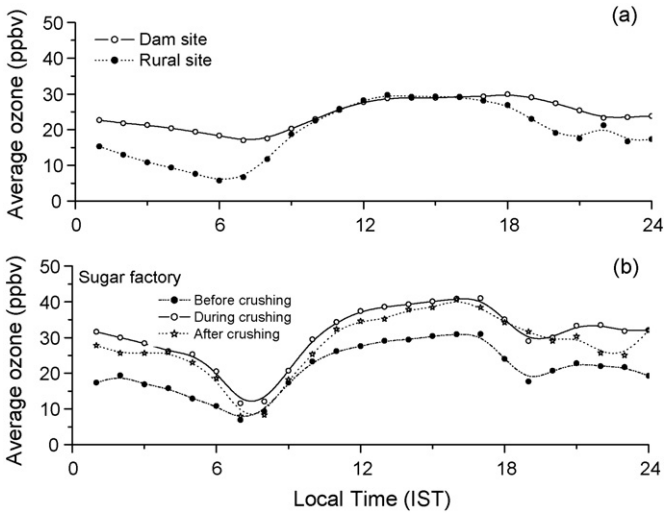

Fig. 8. Diurnal variations in ozone concentration observed near to the dam (a) and in the sugar factory premises (b), indicating higher ozone in the sugar factory premises during crushing and higher ozone in the morning hours near to the dam.

sites appears to be a result of photochemical O_3 destruction during daytime hours in a regime with very low NO_x concentrations [30].

Measurements of O_3 made near to the Mulanagar, dam site shows the loss of O_3 is slower near to the dam than other urban and rural sites during the nighttime. The minimum of O_3 concentration is higher (15–20 ppbv) in the morning hours at sunrise as compared to the other urban and rural sites (5–10 ppbv) during the same period of observation in the present study and earlier studies reported in India [16,17] (Fig. 8a). It appears that O_3 titration was slower during nighttime which results in higher O_3 concentration in the morning hours as compared with the other urban and rural sites. Hence, it is seen from Fig. 8a that diurnal pattern of O_3 was relatively flat near to the dam, which allows to experience ambient environment at higher O_3 levels.

Fig. 8b shows higher O_3 concentrations observed during the crushing period of the sugar factory, as compared to that of before and after the crushing time. During the crushing daily mean of O_3 31 ppbv was observed and after the crushing daily mean decreases to 28 ppbv. The decrease in O_3 concentration after crushing is related to the decrease in precursor gases in the sugar factory premises. This shows that the approximately 11% increase in O_3 concentration during crushing period is attributed to the increase in emissions of precursor gases during working of sugar factory. Therefore, it seems to contribute to enhance O_3 concentration during crushing from November to May in the western plateau of Maharashtra state known as sugar factory belt of India. The increase in O_3 level above 40 ppbv during daylight hours may affect the agricultural winter wheat crop yields over the Indian region [29]. It is expected to reduce winter crop yields by 5% as per the AOT40 concept at the present level of O_3 and it will reduce more if O_3 level increases in near future.

Fig. 9a and b shows the comparison of diurnal variation of O_3 concentration with the diurnal air temperature and relative humidity (RH) at Pune (urban) and Joharapur (rural) measured during summer month in April 2005. It shows that O_3 increases with increase of temperature in the daytime, while it decreases with increase of RH at both the urban and rural sites. However, it is also seen from Fig. 9 that daytime O_3 concentration is higher by about 25 ppbv due to high precursor gases at urban site than the O_3 at rural site. Fig. 10a–f shows the average monthly O_3 variation with the meteorological parameters (temperature, relative humidity (RH),

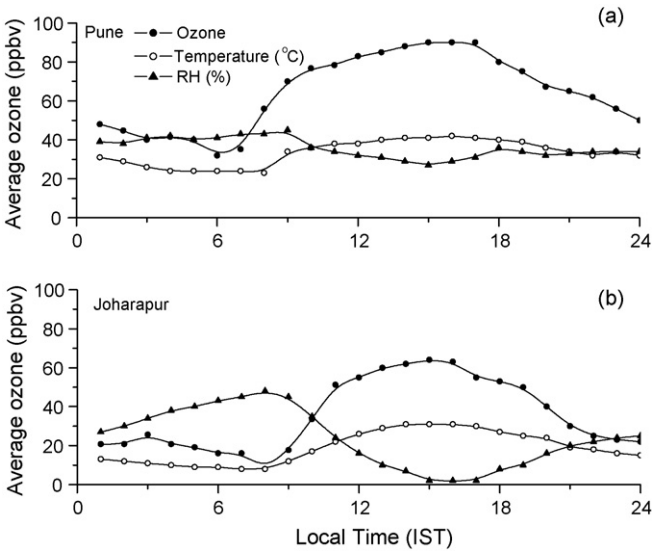

Fig. 9. Variation of diurnal ozone concentration with temperature and relative humidity (RH) observed during summer in April 2005 at (a) urban site, Pune and (b) at rural site, Joharapur.

rainfall (RF), cloud cover (CC), and wind speed (WS)) observed at Joharapur. It is seen from Fig. 10a, b and e that O_3 increases with the increase of temperature and it decreases with the increase of CC, which is similar with the our previous study of O_3 reported at coastal site, Tranquebar (11°N, 79.9°E, 9 m asl) by Debaje et al. [32].

3.3. Wind pattern

The wind pattern is traced and studied by using 3D 7 days back trajectories from HYSPLIT-4 model (website: http://www.arl.noaa.gov/ready/hysplit4.html) over Pune (here trajectories figures are not included). In general, flow pattern in the boundary layer winds is southwesterly during the monsoon season from June to September over the Indian subcontinent, and brings cleaner and moist air from the Arabian Sea. On the contrary, the flow becomes exactly opposite in direction northeasterly during the winter and summer season from December to May and carries significant amounts of air pollutants from the northeast continental region of India over the study region. Fig. 11 shows the variation of O_3 concentration with the variation in the direction of wind at Joharapur (wind rose). It is seen from Fig. 11 that changes in the concentration of O_3 are associated with the changes in the direction of wind. The higher O_3 concentration is observed, when wind is from northeasterly; while lower O_3 concentration is observed, when wind flow is southwesterly direction. Khemani et al. [13] and Beig et al. [17] reported similar type of relationship of O_3 with the direction of wind over Pune. This feature indicates that the influence of polluted and clean air wind pattern on the O_3 concentration over the study region.

3.4. Seasonal diurnal variability

Fig. 12a and b shows the average seasonal diurnal variation of O_3 concentrations observed at urban site, Pune (a) and (b) rural site, Joharapur. The highest O_3 41.2 ppbv (38.6 ppbv) was observed during the daytime at Pune (Joharapur) in winter season with well-marked peak in the forenoon (afternoon) as compared to the other seasons. The low boundary layer height traps the precursor gases (NO_x, CO, VOC) near to the ground level in the winter at both urban and rural sites [14,17]. It is to be noted that peak of O_3 concentration was observed always in the afternoon in all seasons in the rural site, whereas it varies with seasons in the urban site. The photochemical production of O_3 was not dominant in winter as compared to that in summer because of low production of odd hydrogen radical's concentration and low intensity of incoming solar radiation to fuel the O_3 formation processes [1,25]. Despite these odd factors significant amount of O_3 was observed in winter season similar to that of summer season and well marked peak in the forenoon hours around 10:00–12:00 h at urban site (Fig. 12a), whereas it was in the after-

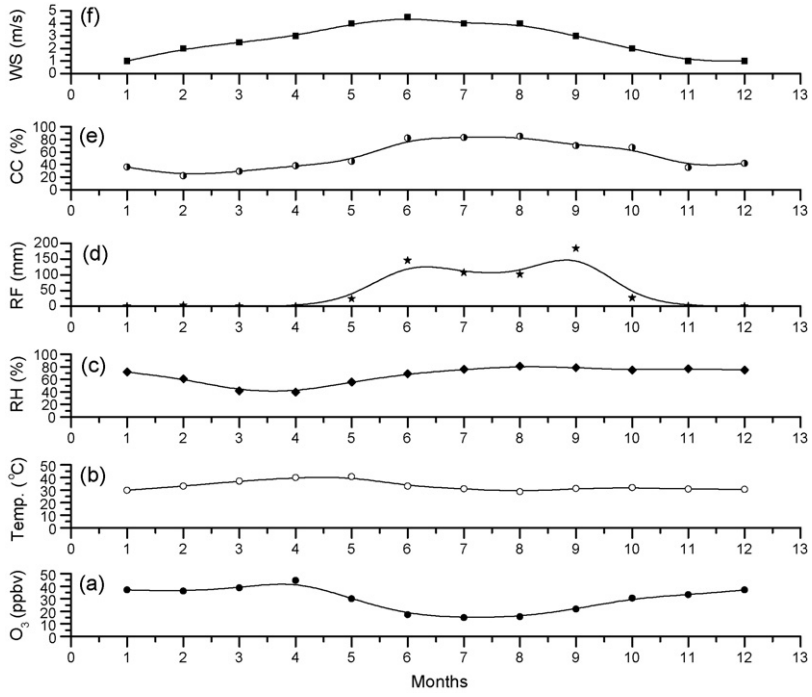

Fig. 10. Seasonal variations in (a) ozone, (b) temperature, (c) relative humidity (RH), (d) rainfall (RF), (e) cloud cover (CC), and (f) wind speed (WS) for 2002–2005 at Joharapur.

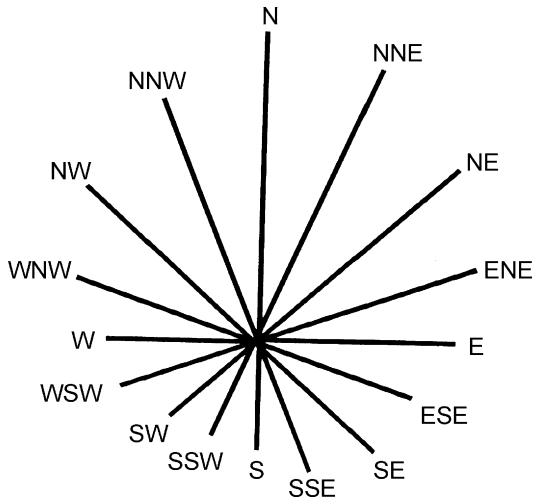

Fig. 11. Variations of the ozone concentrations with that of wind direction (scale: 1 cm = 10 ppbv ozone) observed at Joharapur.

noon around (14:00–16:00 h) at rural site (Fig. 12b). The increase in the lifetime of O_3 during winter is due to decrease in temperature, which causes an accumulation of O_3 over the period of time. Further, Indian region is dominated by an anticyclone in winter with calm wind less than 1 ms^{-1} prevailing stagnant condition over the study region.

The differences in the occurrence of peak of O_3 in the urban and in rural sites appear to be related to the maximum emission of NO_x and hydrocarbons at different times. The time of occurrence of daytime peak in O_3 was different in urban and in rural sites. In the urban site, large emissions of NO_x and hydrocarbons concentration in the morning hours from commuter vehicular traffic that utilized rapidly for production of O_3 as intensity of incoming solar radiation increases ($NO + HO_2 \rightarrow NO_2 + OH$, which further produces O_3 by photolysis of NO_2) [25]. This helps attain pronounced peak O_3 concentration in the forenoon in winter at the urban site. On the contrary, incoming solar radiation intensity increases at noon, while O_3 slightly decreases at noon because of complete utilization of freshly emitted NO_x. In the afternoon as solar intensity decreases, O_3 buildup also decreases, while commuter traffic emission increases which is now responsible for rapid decrease of O_3 level at faster rate at urban site.

On the other hand, in the rural site emission sources of precursor gases are different from that of urban sources and depend more on natural processes such as intensity of incoming solar radiation and air temperature (Fig. 12b). Hence, the emission rate of precursor gases is slower in the rural site as compared to that in urban site. The O_3 concentrations linearly depend on emission of NO_x in the rural sites [33]. On the contrast in the urban, there is a negative relationship of O_3 with NO_x emissions that can also occasionally switch to positive under particular meteorological conditions [34]. The pronounced peak of O_3 was attained always in the afternoon at rural site which corresponds to the peak of air temperature and peak of isoprene emission from crop and trees [35]. The loss of O_3 by NO appears to be less effective at the rural site because of absence of NO_x emission from vehicular traffic that helps to shift the pronounced peak of O_3 in the afternoon.

During summer season high O_3 40.9 ppbv (37.7 ppbv) was observed in the daytime at urban (rural) site as formation of O_3 was more pronounced with warm temperature and intense incoming solar radiation (favorable meteorological conditions for O_3 formation in most urban and polluted rural areas). O_3 concentrations show comparatively less diurnal amplitude variability in rural areas than in the urban due to the absence of high NO_x emission sources. The high O_3 values in summer are related to in situ photochemical production with well-marked peak shifted now in the afternoon

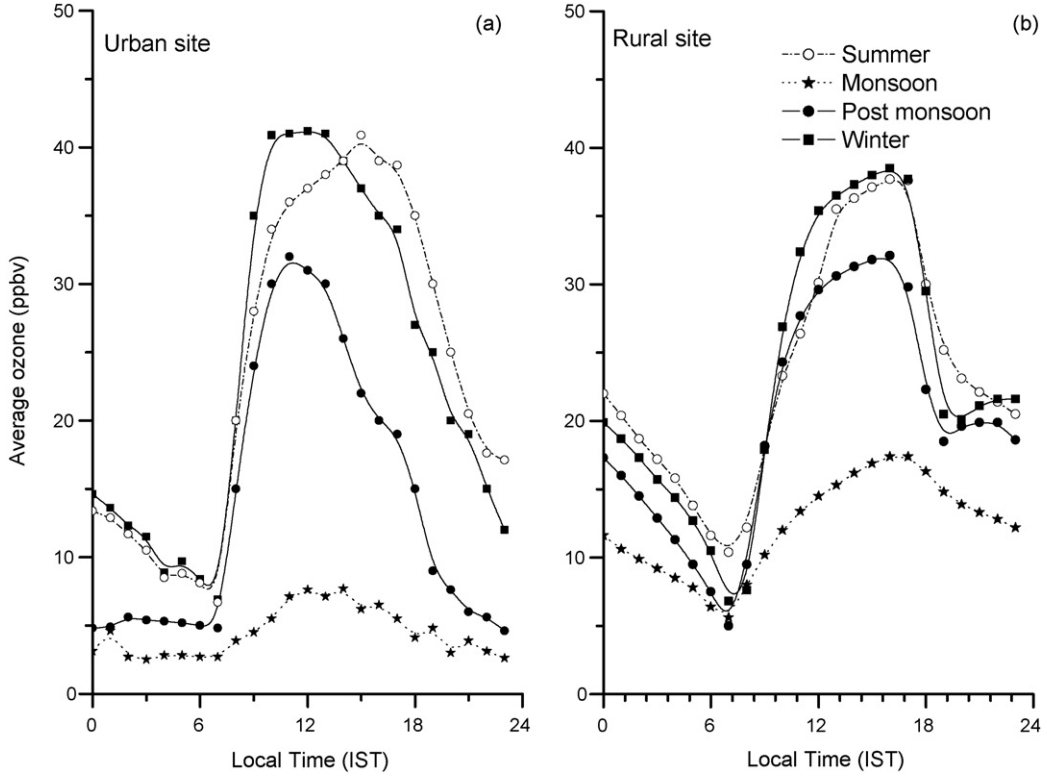

Fig. 12. Seasonal diurnal variability of ozone observed at (a) urban site, Pune and (b) rural site, Joharapur.

(which appeared earlier in the forenoon in winter season) in the urban site. On the contrary, in the rural site, time of occurrence of peak O_3 remained unchanged and was observed strictly in the afternoon. This indicates that diurnal pattern of O_3 was more stable in the rural site than at urban site with respect to season and precursor concentration levels. It seems that sufficient amount of anthropogenic precursor gases get transported from near by cities and sugar factories to the receptor site. The large emission of isoprene and additional biomass burning to make land ready for cultivation were also significant local sources of precursor gases in the rural site [36], which produces significant amount of O_3 nearly equal to the O_3 in the urban site. The diurnal amplitude of O_3 gets reduced some times due to summer shower in some years in the summer season. The comparison of diurnal variations of O_3 in winter and summer season revealed a sharp increase and then sharp decrease in daytime maximum O_3 (shorter peak period: 12:00–17:00 h for O_3 above 35 ppbv) during winter months, whereas the daytime maximum in O_3 broader (longer peak period: 11:00–20:00 h for O_3 above 35 ppbv) is observed during summer months (as shown in Figs. 3 and 4). Therefore, the monthly average of O_3 leads to higher during the summer months instead of in winter months. The daily seasonal diurnal average of O_3 was observed to be higher 23.7 ppbv (24 ppbv) at the urban site than in the rural site 23.3 ppbv (23.6 ppbv) during the winter (summer) season.

In the monsoon season diurnal amplitude of O_3 was low at both rural and urban site due to near absence of incoming solar radiations and large washout of precursor gases by precipitation (Tables 2 and 3). In the cloudy weather in the absence of solar radiation, generation of new odd hydrogen radicals is less, results in slow O_3 formation. Hence, the diurnal amplitude of O_3 was observed to be flat in the monsoon as compared to the winter and summer season (as shown in Figs. 3 and 4). The peak O_3 was observed around (12:00–13:00 h) in the urban site, whereas it was still in the afternoon in the rural site. In the absence/diffuse of incoming solar radiation NO_x plays different roles in the urban and rural sites. It is seen from Fig. 12b that in the rural site relatively higher O_3 level (around 17 ppbv) is observed as compared to in the urban site (8 ppbv). There appears to be less O_3 loss by NO due to low NO_x emission (loss of O_3 < production of O_3). On the contrary, in the urban areas higher emission of NO_x from vehicular traffic decrease O_3 level in the absence of solar radiation resulted in more O_3 loss by NO (loss of O_3 > production of O_3) by the same NO titration reaction (as shown in Fig. 12a, lower curves of solid stars dotted line).

3.5. Seasonal cycle of ozone concentration

Fig. 13 shows the seasonal cycle of O_3 concentration (monthly mean) for 2001–2005 at urban site, Pune (solid lines) and for 2002–2005 at rural site, Joharapur (dotted lines). It is seen from the figure that higher O_3 concentration was observed during the summer months March or April and low concentration during the monsoon months July to August at both the sites. The O_3 concentration increases during early winter season from October with a maximum (30–40 ppbv) during summer season in March or April and decreases during monsoon season from June to September. The main reason for a winter maximum of O_3 due to decrease in temperature which increases the lifetime of O_3 and summer maximum is related to the pronounced photochemical buildup of O_3 due intense solar radiation. The low O_3 concentration (5–15 ppbv) observed during monsoon is due to the decrease in its precursor gases by rain processes and reduce solar radiation at the ground level (Tables 2 and 3). It is seen from Fig. 13 that the higher O_3 concentration is observed at urban site than at the rural site in summer. On the contrary, higher ozone concentration is observed at rural site than at the urban site during the monsoon season (four dotted lines). Fig. 14 (a and b) shows the bar diagram of daytime average maximum O_3 concentration for the study period at Pune and Joharapur. Table 4 shows the summary and comparison of average monthly (seasonal cycle) maximum of O_3 concentration at urban site Pune and rural site Joharapur with the other studies carried out at Pune and rural site Gadanki in India. Measurements of O_3 carried out at other three sites (Bhenad, Mulanagar and Mahabaleshwar) in this study were less than a year, hence, these sites are not included in Table 4. Detailed elaboration has been carried out on diurnal variation of O_3 for these sites discussed in the earlier section. It is seen from Table 4 that the maximum of O_3 was observed during the different month at Pune and at Joharapur, while minimum of O_3 in July or August at both the sites. The maximum of O_3 was observed in a month of April, March, April, February and April for year 2001–2005 at Pune, and in a month of April, April, January and April for year 2002–2005 at Joharapur, respectively. Beig et al.

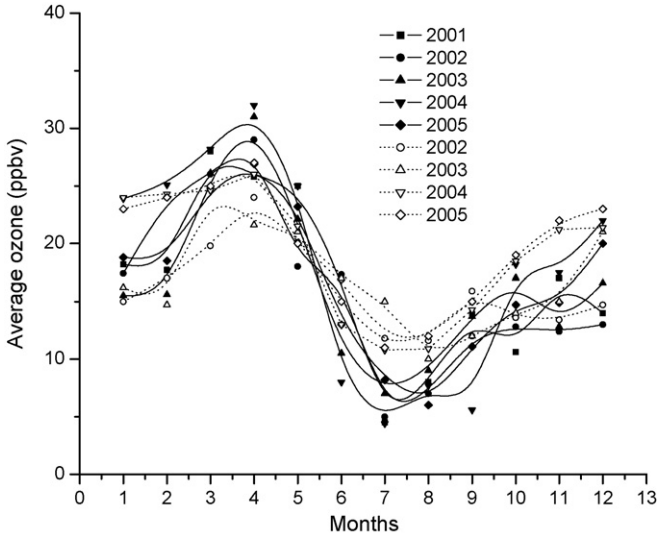

Fig. 13. Average monthly ozone concentration (seasonal cycle) observed at urban site Pune (solid lines) and at rural site Joharapur (dotted lines).

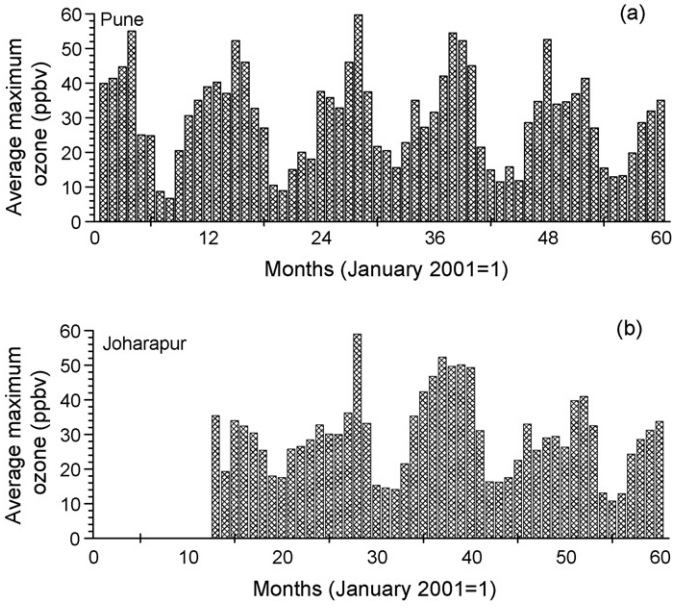

Fig. 14. Average maximum ozone concentration observed in the daytime (a) urban site Pune and (b) rural site Joharapur.

Table 4
Summary and comparison of average monthly maximum concentration of ozone (ppbv) measured in the present study at urban and rural sites with other site measurements available over Indian region

	Pune						Joharapur				Pune[a]	Gadanki[b]
	Statistics	2001	2002	2003	2004	2005	2002	2003	2004	2005	2003–04	1993–96
January	Mean	39.9	40.3	35.8	42	33.9	35.4	30.3	52.3	29.4	37.6	26.2
	S.D.	12	10	6	11	7	4	5	5	4	16	14
February	Mean	41.4	37	32.5	54.5	34.6	19.3	30	49.6	26.3	54.6	30.1
	S.D.	10	6	6	11	11	3	4	8	5	15	17
March	Mean	44.7	52.2	46.1	52.2	36.9	34	36.2	50.1	39.8	52.5	33.6
	S.D.	9	8	12	11	9	6	6	6	4	16	21
April	Mean	55	46.1	59.7	45	41.4	42.4	58.9	49.3	41	42.5	24.7
	S.D.	16	11	13	12	15	5	18	9	5	9	16
May	Mean	25	32.7	37.4	21.4	27.1	30	33.2	31.1	32.5	27.5	24.9
	S.D.	13	9	12	5	7	9	12	6	6	4	11
June	Mean	24.8	27.1	21.7	14.9	15.5	25.4	15.3	16.3	13.1	20.4	25.9
	S.D.	7	9	6	4	3	7	2	5	4	2	8
July	Mean	8.7	10.5	20.4	11.5	12.9	18	14.5	16.2	10.8	17.5	20.3
	S.D.	2	3	4	3	2	3	3	3	2	5	7
August	Mean	6.7	8.9	15.6	15.8	13.3	17.6	14.1	17.5	12.9	12.2	18.5
	S.D.	2	2	2	2	2	2	2	2	1	7	6
September	Mean	20.5	15	22.8	11.8	19.8	25.7	21.5	22.6	24.3	14.9	19.8
	S.D.	10	4	7	2	5	6	3	5	3	5	11
October	Mean	30.6	20	35	28.6	28.5	26.5	35.3	33	28.5	25	18.1
	S.D.	12	5	10	8	6	5	7	4	9	15	11
November	Mean	35	18.1	27.2	34.7	31.9	28.4	42.3	25.4	31.2	32.5	26.1
	S.D.	13	4	7	9	6	5	7	7	6	20	14
December	Mean	38.9	37.6	31.6	52.6	35	32.7	46.7	29	33.7	34	30
	S.D.	12	3	7	17	10	6	7	7	6	18	15
Annual	Mean	31	28.7	32.2	32.1	27.6	28	31.5	32.7	27	30.9	24.9
	S.D.	10	6	8	8	7	5	6	6	5	11	14

[a] June 2003–May 2004 for Pune [17].
[b] 1993–1996 for rural site Gadanki [16].

[17] reported maximum of O_3 in February and minimum of O_3 in August for the 1-year period June 2003–May 2004 at Pune, similar with the our present O_3 measurements at Pune. Similarly, Naja and Lal [16] reported maximum of O_3 in March at Gadanki, while in January or April at Joharapur. On the contrary, minimum of O_3 is reported in October at Gadanki due to the northeast monsoon period October–December over this region instead of in July or August (southwest monsoon, as shown in Fig. 4) as observed in the present measurements at Joharapur. Debaje et al. [32] reported minimum of O_3 in October at coastal site Tranquebar due to the northeast monsoon, similar with the minimum of O_3 observed at Gadanki. The annual average for 5 and 4 year's measurements show maximum O_3 concentration was around 30.3 ± 8 and 29.8 ± 6 ppbv in urban and rural sites, respectively.

3.6. Model versus observations

Comparison of the simulated diurnal and monthly O_3 concentration with the measured O_3 concentration at Pune latitude by using a Eulerian photochemical model is shown in Fig. 15a and b. Fig. 15a shows that the model diurnal variation of O_3 in winter January 2004 is compared with the corresponding measured diurnal variation of O_3. The measured diurnal variations of O_3 show maximum O_3 concentration 40–50 ppbv around 12:00 h and minimum concentration 5–10 ppbv at the sunrise. Model O_3 maxima and minima follow O_3 measurements pattern. The diurnal pattern of O_3 is reproduced well by the model; however, model values are less by 15–25% at the daytime and

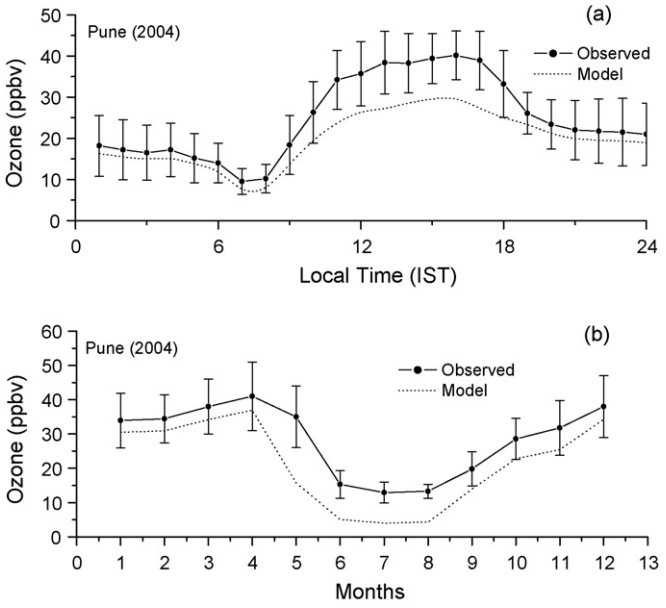

Fig. 15. Comparison of observed concentration of ozone with the concentration simulated from a Eulerian photochemical model (a) diurnal and (b) seasonal variation for 2004 at Pune. Vertical bars are 1σS.D.

nighttime O_3 values are less by 5–15% than the measured O_3 values [24]. The important feature in our result is that model O_3 follows general diurnal features by using photostationary state relation. This means that we are able to model diurnal variation pattern, maxima and minima of O_3 up to a certain extent.

Fig. 15b shows the average monthly (seasonal cycle) variation of measured O_3 versus model O_3 for the year 2004. Model O_3 values follow general monthly features of measured O_3 values. It is seen from Fig. 15b that measured O_3 values are higher by 20–30% than the model O_3 values. The large difference (25–40%) in O_3 concentration is observed during the monsoon season between model and observed O_3, while less difference (10–20%) during winter and summer months. These differences in O_3 values are expected in the troposphere considering the O_3 formation and destruction mechanism involving simple chemistry (photostationary state relation). The present model results help to understand the mathematical modeling response of photochemical processes to surface O_3 and its precursor level in the troposphere over the Indian region.

3.7. Comparison with other measurements

3.7.1. Diurnal variations

The diurnal variations of O_3 observed at these five different sites, which are highly influenced by the seasonal changes, as like some other sites in India. The diurnal patterns indicating that O_3 concentration starts increasing after sunrise, attains maximum value during noontime and then decreases have been observed at an urban site, Pune by Khemani et al. [13] and Beig et al. [17]. The daytime increase in O_3 concentration, which is a pronounced feature of an urban polluted site, is basically due to the photoxidation of the precursor gases. The diurnal variation in O_3 is the result of the photochemical production of O_3 and O_3 loss by dry deposition and reaction with NO (titration), where the emission of precursor gases controlled by vehicular traffic and industrial activity. Earlier O_3 studies at Pune by Tiwari and Peshin [26] show the minimum in the O_3 concentration (2–5 ppbv) occurs at about 07:00–08:00 h local time and maximum (23–27 ppbv) in late afternoon between 14:00 and 16:00 h local time during the year 1974–1985, and thereafter maximum (32–35 ppbv) shifted to forenoon between 10:00 and 12:00 h during the year 1988–1991 during winter. This indicates that, earlier diurnal variation of O_3 was dominated by air temperature, but now it is dominated by precursor gases. Diurnal variations in O_3 at Delhi (28.35°N, 77.12°E) by Jain et al. [37] have shown minimum concentration in the morning and maximum concentration at the noontime, similar to O_3 measurements in the present study at Pune. At high altitude Himalayan site, the higher values of surface O_3 during nighttime than daytime have shown by Ali et al. [38] at Kothi (32.31°N, 77.18°E, 2530 m asl), in northern India, which has been attributed to mixing from upper layer. Similar type of diurnal variations in O_3 concentration has been shown by Naja et al. [30] at Mt. Abu high altitude mountain site (as shown in Fig. 7), but the same maximum O_3 concentration during nighttime in the present study at Mahabaleshwar is attributed to the transport from nearby cities. In sugar factory burning lots of baggasse (a fine sugarcane residue) for heating boiler during the operation emits large-scale pollutant precursor gases. The large biomass burning during March to May in the Indian subcontinent region [20,36], results in maximum emission of NO_x, CO (see Table 3) and hydrocarbons lead to more photochemical buildup of O_3. Beig et al. [17] reported that increase of pollutants (NO_x, CO and O_3) to the receptor site at Pune during the working period of sugar factories. In the present study, increase of O_3 concentration was observed at Bhenda, sugar factory (Fig. 8b), which was in agreement with the O_3 observation reported by Beig et al. [17] at Pune.

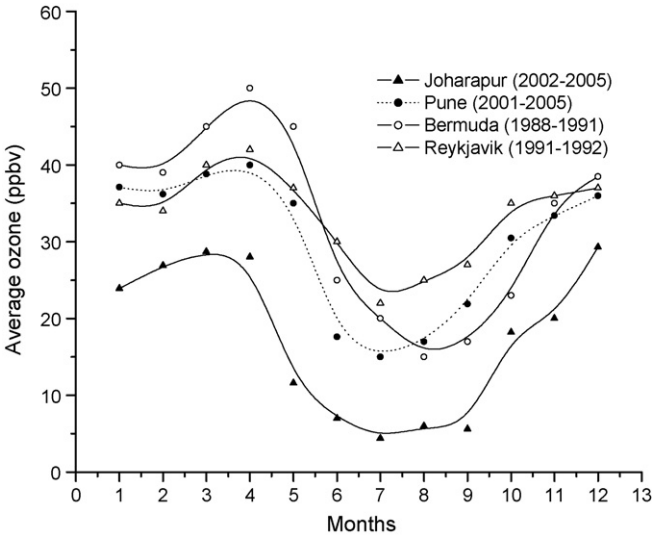

Fig. 16. Average monthly ozone concentrations at Joharapur and Pune compared with those of at Bermuda and Reykjavik.

Measurements made at Ahemdabad over northwest India show higher O_3 concentration during February [15]. They have attributed these higher levels to low convective mixing and stagnant wind patterns. On the contrary measurements made at Delhi show high O_3 during the summer month of May, however, summer time high O_3 at Delhi is explained on the basis of large photochemical O_3 production, which is similar to high O_3 concentration in the present study during April at urban site, Pune (Fig. 3). Earlier studies carried out at Pune show the high O_3 concentration during the month February to April and low O_3 concentration during the monsoon season [13,17,26], similar with the present study.

3.7.2. Seasonal variations

Measurements of O_3 made at Pune and Joharapur are compared with the O_3 reported at Bermuda (32°N, 65°W) and Reykjavik (64°N, 22°W) (Fig. 16) [39,40]. It is seen from Fig. 16 that the O_3 concentration observed at Pune and O_3 concentration reported at Reykjavik show the nearly similar O_3 seasonal cycle. The lower O_3 is observed at Joharapur than the O_3 at Bermuda, however, seasonal pattern of O_3 is similar at both the site. Higher O_3 is observed during summer March or April, and low O_3 from July to September at all four sites. The seasonal cycle of O_3 at Pune and Joharapur is controlled by local pollution and photochemical buildup, whereas at Bermuda and Reykjavik it is controlled by natural processes such as downward transport of stratospheric ozone. Further, O_3 chemistry at Bermuda and Reykjavik is dominated by photochemical destruction of O_3 in the daytime hours due to the low NO_x concentration, i.e. minimum of O_3 in the daytime due to lack of photochemical buildup and maximum of O_3 during the nighttime. From the last 2–3 decades, significant changes have occurred from 1974s to 1991s in the seasonal variation of O_3 at Pune [26]. The daytime maximum of O_3 concentration has increased from 23 ppbv in 1974 to 35 ppbv in 1991. At present, daytime maximum of O_3 exceeds very often 80 ppbv in February to April, which was 25–30 ppbv during the year 1973 at Pune. This indicates that precursor gases load has increased extensively. Khemani et al. [13] reported daily average value of O_3 between 13.5 and 15.4 ppbv during the year 1992 in the forest areas of Nilgiri Biosphere Reserve in Tamil Nadu, India; which was lower than the present O_3 values (25.6 ppbv) measured near to the Mulanagar Dam.

Average maximum O_3 concentration observed at these five sites was low between 40 and 50 ppbv as compared to that many global

sites such as northern United States, Mexico, Europe, Canada, and also Taiwan, where hourly average O_3 concentrations exceeding 100 ppbv for many days have been commonly observed [40,41]. However, there are few instances of hourly average peak O_3 concentration in February to April at the present urban site which reaches up to 90 ppbv alarming by air quality standard. The low O_3 at these sites as compared to that of the above global sites was attributed to the low precursor gas concentrations which are responsible for low photochemical production of O_3. It has been shown recently during Indian Ocean Experiment from January to March 1999 that the ratio of total CO and hydrocarbons sources (S_C) and combined anthropogenic NO_x sources (S_N), i.e. S_C/S_N, is more than four times higher in India ($S_C/S_N = 21.5$) than in North America ($S_C/S_N = 4.96$). Similarly, S_C/S_N ratios for Europe, China and East Asia are 6.6, 11.6 and 14.1, respectively. This infers that O_3 photochemistry in India is strongly NO_x limited, which indicates that O_3 production increases with the increase of NO_x concentration [42]. The efficiency of O_3 production (number of O_3 molecules formed per NO_x molecule lost) is highly non-linear, depending on the amount of NO_x present and on the ratio of S_C/S_N in the atmosphere. Berntsen et al. [43] predicted that for Indian region the O_3 production efficiency is much higher, 100 ppbv/Tg (N) per year than the Japan (8.4) and China (6.5). This is due to the significantly lower NO_x concentrations over the Indian region. Further, considering the present IPCC scenario the NO_x concentration is increasing at the rate of about 5% per year in India for year 2000–2100, and 3.3% per year over East Asia indicate higher production of O_3 over Indian region in near future [12].

4. Conclusions

Simultaneous measurements of surface O_3 at five different sites with different atmospheric conditions in western Maharashtra, India between 2001 and 2005 have provided a valuable data set for this region. Diurnal and seasonal scale of O_3 concentration is a function site, due to the different rate of emission of precursor gases and transport. Variability in O_3 mainly influences by in situ photochemistry of O_3 production at urban and rural sites and by transport at mountain site. The average high maximum of O_3 concentration 49.5 ± 13 ppbv was observed during summer in April, whereas low maximum of 12.1 ± 2 ppbv during the monsoon in August in the urban site. On the contrary, corresponding nearly equal high maximum concentration of O_3 47.9 ± 9 ppbv and low maximum of 15.6 ± 2 was observed in the rural sites indicates the rise in anthropogenic pollution in rural areas. It suggests that equally high concentration of O_3 in the rural areas is due to the increase of precursor gases load by transport from nearby urban cites into the rural areas and also increase of human activities in particular sugar industries and biomass burning over this region.

The high O_3 concentrations with low solar radiation and low temperature during winter season January or February suggest the influence of minimum temperature which increases the life time of O_3 and trapping near to the ground due to low mixing height. On the contrary, high O_3 during summer in March or April indicates the influence of in situ photochemical production of O_3 as rate of chemical reaction increases with the temperature due to intense solar radiation. This rise in air pollutants (O_3) in the rural areas may cause significant agricultural crops yield consequences in near future.

A comparison of measured diurnal and monthly averaged O_3 with that of a Eulerian photochemical model simulated results are in good agreement with 20–30% difference. This is due to the simple physical and chemical mechanism involved in the model. Cloud processes and nighttime chemistry are some of the major factors, which are responsible for more disagreement in O_3 simulation in monsoon season. The simulated and observed O_3 show the better agreement during winter and summer season. For further study, simultaneous measurements O_3 and its precursor gases at many places (network) are needed for detailed understanding of the variability of O_3 over the Indian region.

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References

[1] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics From Air Pollution to Climate Change, John Wiley and Sons, Inc., New York, 1998, pp. 234–336.
[2] S.C. Liu, M. Trainer, F.C. Fersenfeld, D.D. Parrish, E.J. Williams, D.W. Fahey, G. Hubler, P.C. Murphy, Ozone production in the rural troposphere and the implications from regional and global ozone distributions, J. Geophys. Res. 92 (1987) 4191–4207.
[3] R. Vingarzan, A review of surface ozone background levels and trends, Atmos. Environ. 38 (2004) 3431–3442.
[4] M. Lippmann, Health effects of ozone, Air Waste Manage. Assoc. 39 (1989) 672–695.
[5] J.A. Mulholland, A.J. Butler, J.G. Wilkinson, A.G. Russeell, Temporal and spatial distributions of ozone in Atlanta: regulatory and epidemiologic implications, J. Air Waste Manage. Assoc. 48 (1998) 418–426.
[6] P.H. Fischer, B. Brunekreef, E. Lebret, Air pollution related deaths during the 2003 heat wave in the Netherlands, Atmos. Environ. 38 (2004) 1083–1085.
[7] J.R. Stedman, The predicted number of air pollution related deaths in the UK during the August 2003 heatwave, Atmos. Environ. 38 (2004) 1087–1090.
[8] J.L.S. Fuhre, M.R. Ashmore, Critical levels for ozone effects on vegetation in Europe, Environ. Poll. 97 (1997) 91–106.
[9] W.L. Chameides, et al., Is ozone pollution affecting crop yields in China? Geophys. Res. Lett. 26 (1999) 867–870.
[10] Z.-W. Feng, M.-H. Jin, F.-Zh. Zhang, Y.-Z. Huang, Effects of ground-level ozone [3(O] pollution on the yields of rice and winter wheat in the Yangtze River Delta, J. Environ. Sci. (China) 15 (2003) 360–362.
[11] M.W.M. Hisham, D. Grosjean, Sulfur dioxide, hydrogen sulfide, total reduced sulfur, chlorinated hydrocarbons and photochemical oxidants in Southern California Museums, Atmos. Environ. A25 (1991) 1497–1505.
[12] IPCC (Intergovernmental Panel on Climate Change) Climate Change, The Scientific Basis, Cambridge Univ. Press, 2001, pp. 239–287.
[13] L.T. Khemani, G.A. Momin, P.S.P. Rao, R. Vijaykumar, P.D. Safai, Study of ozone behaviour at urban and forested sites in India, Atmos. Environ. 29 (1995) 2021–2024.
[14] S. Lal, M. Naja, B.H. Subbaraya, Seasonal variations in surface ozone and its precursors over an urban site in India, Atmos. Environ. 34 (2000) 2713–2724.
[15] L.K. Sahu, S. Lal, Distributions of C2-C5 NMHCs and related trace gass at a tropical urban site in India, Atmos. Environ. 40 (2006) 880–891.
[16] M. Naja, S. Lal, Surface ozone and precursor gases at Gadanki (13.5°N, 79.2°E), a tropical rural site in India, J. Geophys. Res. 107 (D14) (2002), doi:10.1029/2001JD000357.
[17] G. Beig, S. Gunthe, D.B. Jadhav, Simultanous measurements of ozone and its precursors on a diurnal scale at a semi urban site in India, J. Atmos. Chem. 57 (2007) 239–253.
[18] IMD (India Meteorological Department), Indian Daily Weather Report, for the period 2001–2005.
[19] TCO (Transport Commissioner's Office), Motor Transport Statistics Report 2003–2004, pp. 42–91, Maharashtra State, Mumbai, India, 2004.
[20] A. Garg, R.P. Shukla, S. Bhattacharya, V.K. Dadhwal, Sub-region (district) and sector level SO_2 and NO_x emissions for India: assessment of inventories and mitigation flexibility, Atmos. Environ. 35 (2001) 703–713.
[21] D.G. Streets, T.C. Bond, G.R. Carmichael, S.D. Fernandes, Q. Fu, D. He, Z. Klimont, S.M. Nelson, N.Y. Tsai, M.Q. Wang, J.-H. Woo, K.F. Yarber, An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, J. Geophys. Res. 108 (2003) 8809, doi:10.1029/2002JD003093.
[22] C.R. Sreedharan, V.S. Tiwari, The use of a Brewer bubbler as continuous ozone sensor, J. Phys. E. Sci. Inst. 4 (1971) 706–707.
[23] WMO (World Meteorological Organization), Third WMO inter-comparison of the ozonesonde used in the Global Ozone Observing System (Canada, 13–24 May, 1991). Global Atmospheric Watch, Rep. 27, Geneva, Switzerland, 1994.

[24] S.B. Debaje, D.B. Jadhav, An Eulerian photochemical model for tropospheric ozone over the tropics, Curr. Sci. 77 (1999) 1537–1541.
[25] H.E. Jeffries, Photochemical air pollution, in: H.B. Singh (Ed.), Composition, Chemistry and Climate of the Atmosphere, Van Nostrand Reinold Publication, New York, 1995, pp. 308–348.
[26] V.S. Tiwari, S. Peshin, A prominent maximum in surface ozone concentration during winter months at Pune (India), Mausam 46 (1995) 155–162.
[27] G. Petron, P. Harley, J. Greenberg, A. Guenther, Seasonal temperature variations influence isoprene emission, Geophys. Res. Lett. 28 (2001) 1707–1710.
[28] P.J. Curtzen, Ozone in the troposphere, in: H.B. Singh (Ed.), Composition, Chemistry and Climate of the Atmosphere, Van Nostrand Reinold Publication, New York, 1995, pp. 349–393.
[29] M.L. Mittal, P.G. Hess, S.L. Jain, B.C. Arya, C. Sharma, Surface ozone in the Indian region, Atmos. Environ. 41 (2007) 6572–6584.
[30] M. Naja, S. Lal, D. Chand, Diurnal and seasonal variabilities in surface ozone at a high altitude site Mt. Abu (24.6°N, 72.7°E, 1680 m asl) in India, Atmos. Environ. 37 (2003) 4205–4215.
[31] L. Gallardo, J. Carrasco, G. Olivares, An analysis of ozone measurements at Cerro Tololo (30°S, 70°W, 2200 m a.s.l.) in Chile, Tellus 52B (2000) 50–59.
[32] S.B. Debaje, S. Johnson Jeyakumar, K. Ganesan, D.B. Jadhav, P. Seetaramayya, Surface ozone measurements at tropical rural coastal station Tranquebar, India, Atmos. Environ. 37 (2003) 4911–4916.
[33] T. Wang, V.T.F. Cheung, M. Anson, Y.S. Li, Ozone and related gaseous pollutants in the boundary layer of eastern China: overview of the recent measurements at a rural site, Geophys. Res. Lett. 28 (2001) 2373–2376.
[34] C. Honore, R. Vautard, M. Beekmann, Photochemical regimes in urban atmospheres: the influence of dispersion, Geophys. Res. Lett. 27 (2000) 1895–1898.
[35] A. Borbon, H. Fontaine, N. Locoge, M. Veillerot, J.C. Galloo, Developing receptor-oriented methods for non-methane hydrocarbon characterization in urban air. Part II. Source apportionment, Atmos. Environ. 37 (2003) 4065–4076.
[36] M. Galanter, M. Levy II, G.R. Carmichael, Impact of biomass burning on tropospheric CO, NO_x and O_3, J. Geophys. Res. 105 (2000) 6633–6653.
[37] S.L. Jain, B.C. Arya, A. Kumar, S.D. Ghude, P.S. Kulkarni, Observational study of surface ozone at New Delhi, India, Int. J. Remote Sens. 26 (2005) 3515–3526.
[38] K. Ali, G.A. Momin, P.D. Safai, D.M. Chate, P.S.P. Rao, Surface ozone measurements over Himalayan Region and Delhi, North India, J. Radio Space Phys. 33 (2004) 391–398.
[39] S.J. Oltmans, H. Levy II, Seasonal cycle of surface ozone over the western North Atlantic, Nature 358 (1992) 392–394.
[40] S.J. Oltmans, H. Levy, Surface ozone measurements from a global network, Atmos. Environ. 28 (1994) 9–24.
[41] Z. Wang, W. Sha, H. Ueda, Numerical modeling of pollutant transport and chemistry during a high-ozone event in northern Taiwan, Tellus 52B (2000) 1189–1205.
[42] J. Lelieveld, P.J. Crutzen, V. Ramanathan, M.O. Andreae, C.A.M. Brenninkmeijer, T. Campos, G.R. Cass, R.R. Dickerson, H. Fischer, J.A. de Gouw, A. Hansel, A. Jefferson, D. Kley, A.T.J. de Laat, S. Lal, M.G. Lawrence, J.M. Lobert, O.L. Mayol-Bracero, A.P. Mitra, T. Novakov, S.J. Oltmans, K.A. Prather, T. Reiner, H. Rodhe, H.A. Scheeren, D. Sikka, J. Williams, The Indian Ocean experiment: widespread air pollution from south and southeast Asia, Science 291 (2001) 1031–1036.
[43] T. Berntsen, I.S.A. Isaksen, W. Wang, X. Liang, Impacts of increased anthropogenic emissions in Asia on tropospheric ozone and climate, Tellus 48B (1996) 13–32.