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Measurements of Surface Ozone in Rural Site of India

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Abstract

It is known that the formation of surface ozone (O_3) is chemically linked to the emissions of major precursor gases, nitrogen oxides (NO_x) and volatile organic compounds (VOC). This chemical interdependence is highly complex and gives rise to non-linear and coupled pollutant formation processes. In the present study, an attempt has been made to examine the governing photochemical processes of O_3 formation in a rural site. For this purpose, measurements of O_3 and selected meteorological parameters have been made at Joharapur (19.3^o N, 75.2^o E, 474 m above sea level), a tropical rural site in India since March 2002. The annual average diurnal variation of O_3 shows that maximum O_3 concentration is 29.9 ± 5.7 ppbv at noon and minimum 7.0 ± 3.4 ppbv in the morning with 1 σ standard deviation. The monthly average high (low) O_3 44.7 ± 10.8 ppbv (15.0 ± 3.2 ppbv) at noon in April (July), due to possible increase in precursor-gas concentrations by anthropogenic activity and the influence of meteorological parameters. Furthermore, O_3 concentration has been observed as a function of season, which shows that the seasonal highest O_3 concentration is 37.7 ± 8.7 ppbv at noon in premonsoon and lowest 17.4 ± 3.7 ppbv in monsoon season. The hourly averaged O_3 concentration can exceed 70-80 ppbv in premonsoon and winter which is alarming attainment of air quality standard (80 ppbv) over the rural site in India.

Keywords: Ozone production; Meteorological parameters; Rural site; Precursor gases; NO_x titration.

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INTRODUCTION

Atmospheric ozone (stratospheric and tropospheric) plays a critical role in maintaining ecosystems on the earth's surface. Ozone can be either a good thing or a bad depending on where the ozone is and how much there is of it. Surface- or ground-level ozone (O_3) concentration has increased since from the 19th century from about 10 ppbv (parts per billion by volume) at mid-latitudes over Europe and 5 ppbv in tropical regions, with little variation throughout the year (Mickley *et al.*, 1999). Measurements show that O_3 concentration over the urban site in India was about 15 ppbv in the year 1954-55 (Naja and Lal, 1996). The Intergovernmental Panel on Climate Change (IPCC, 2001) has projected increases in O_3 to about 84 ppbv by year 2100 under business-as-usual scenarios, threatening attainment of air quality standards (80 ppbv) over most metropolitan and even rural areas. Increased O_3 concentration is related to the increase in fossil fuel consumption in the automobile, power generation and industrial sectors all over the world to meet the increasing energy demand of the growing population (Levy II H *et al.,* 1997). Ozone is a toxic to humans and phytotoxic to vegetation (Bates, 1994). Chameides *et al.* (1999) observed a decrease in the wheat crop yield in China due to an increase in O_3 (above 60 ppbv) at the ground-level during the China-map experiment. O_3 is also regarded as one of the powerful oxidizing agents causing rapid deforestation and reducing life span of various materials (Hisham and Grosjean, 1991). It plays a key role in the complex oxidation chemistry of the carbon compounds in the lower troposphere and also acts as an important greenhouse gas in the upper troposphere (IPCC, 2001). The dependence of O_3 concentrations on its precursors, particularly nitrogen oxides (i.e., NO_x, NO + NO_2), hydrocarbon reactivity, and radical production rate is highly nonlinear (Liu *et al.*, 1987). O_3 is produced photochemically, when enough NO_x (above 50 pptv, depends on O_3 concentration) is present, by NO_2 photolysis, following oxidation of NO to NO_2 by peroxy radicals (HO_2 and RO_2) (Seinfeld and Pandis, 1998). The high reactivity of NO_x and the associated short photochemical lifetime result in extremely low NO_x concentrations in the troposphere (Logan, 1983). Because the lifetime of NO_x is substantially shorter than other O_3 precursors, such as carbon monoxide (CO) and hydrocarbons, NO_x is often considered as the rate-limiting precursor for O_3 formation. In other words, photochemical production of O_3 is usually proportional to the abundance of NO_x in the tropics. As a result, emissions of NO_x can often lead to significant increase in O_3.

The growing importance of photochemical production of O_3 in the tropical region, such as the Indian subcontinent, is due to intense solar radiation and higher water content in the atmosphere along with increasing NO_x (Andreae and Crutzen, 1997; Lelieveld *et al.,* 2001). Gerg *et al.* (2001) estimated that the rate of increase of NO_x is 5.5%/yr in India, which relates to the economic growth of the nation. Economic sector contributions (1995 inventory) are dominated by the transport (32%) and power generation (28%) sectors, while industry and biomass burning both

contribute 19%. The increase in NO_x concentration is responsible for increasing O_3 on the Indian subcontinent (van Aardenne *et al.*, 1999; Berntsen *et al*., 1996; Debaje *et al.*, 2003). The high variability of precursor gases at local scales with the above nonlinear O_3 production factors necessitates measurements at rural sites.

A few scattered O_3 measurements are available over urban sites (Khemani *et al.*, 1995; Lal *et al.*, 2000) and at the rural site, Gadanki (Naja and Lal, 2002) in India. However, all these studies seldom describe any variation of O_3 at a rural site except at Gadanki, which is located in southeast India about 800 km away from the present O_3 measurement site. In this paper, we present O_3 measurements which have been carried out for the first time in this region at Joharapur, a rural site in western India. Diurnal and seasonal variability in O_3 concentrations have been examined in the light of seasonal changes in meteorological parameters and its precursor gases.

OBSERVATION SITE AND GENERAL METEOROLOGY

The observation site Joharapur is located in western India. Joharapur's population was less than 2,500 in 2001 (Fig. 1). The industrial city Mumbai (19.1^{o}N, 72.9^{o}E, 11 m) is about 300 km to the west and Aurangabad (19.9^{o}N, 75.3^{o}E, 581 m) is 80 km northeast of Joharapur. Both contribute to the enhancement of O_3 precursor gases in these areas. The most prominent meteorological feature a Joharapur is the monsoonal rainfall activity (June-September) amounting to 80% of the total normal annual rainfall (62 cm) (IMD, 2004), which is mostly related to the diurnal and seasonal variation of O_3. Southwest winds bring the monsoon, which sets in by the first week of June and lasts until September (Asanani, 1993). The weather during post monsoon (October-November) is calm and scattered rainfall sometimes occurs. Fair weather conditions prevail during winter season (December-February) with calm wind speeds on the order of 1-2 m/s with northeasterly direction, clear sky and moderate relative humidity of 20-70%. The premonsoon season (March-May) experiences hot weather due to intense solar radiation. The surface air temperature maximum is about 42℃ at noon and minimum 20℃ in the morning.

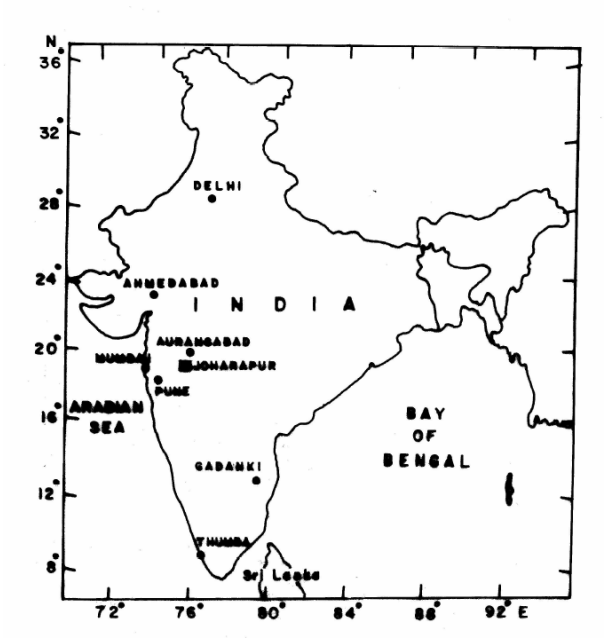

Fig. 1. Location map of the rural site Joharapur, India.

Measurement techniques

A modified Brewer electrochemical ozone sensor developed by the India Meteorological Department (IMD) is used to measure O_3 concentration. The procedure of operation, the working principle of the instrument and other details are given by Sreedharan and Tiwari (1971). This modified electrochemical ozone sensor has been used for continuous O_3 measurements since March 2002 using a strip-chart recorder. The ozone sensor has been calibrated with a UV photometric ozone analyzer (Model O_3 42 M, Environment S. A., May 2002) by running them together with an average time interval of 1 h. Correlation coefficient for O_3 above 1 ppbv for both the instruments is found to be 0.85. The UV ozone analyzer has a minimum detectable limit of about 1 ppbv with a response time 50 s. All times are given in Indian Standard Time (IST), which is ahead of GMT by 5.5 hours. The continuous air temperature and relative humidity (RH) are also measured using thermo-hygrographs. The cloud cover, wind speed, and direction data are used from Indian Daily Weather Report (IDWR), IMD for the years 2002-04.

RESULTS AND DISCUSSION

Fig. 2 shows the frequency distribution of O_3 concentrations (ppbv) in different ranges for the study period (March 2002 - December 2004) at Joharapur (bar diagram). It shows that 60% of all O_3 measurements lie in the range of 0-20 ppbv and remaining 40% in the range 20-70 ppbv (total data points are 8786). It also shows that the highest 21% of all O_3 measurements lies in 10-15

ppbv range, and the lowest 2% in the 50-70 ppbv range. It is important to note that 1-h average O_3 exceeds air quality standards at noon on few occasions in the premonsoon (hot) season in 2003. The results of the diurnal variation of O_3 and variations in different seasons are presented and discussed below.

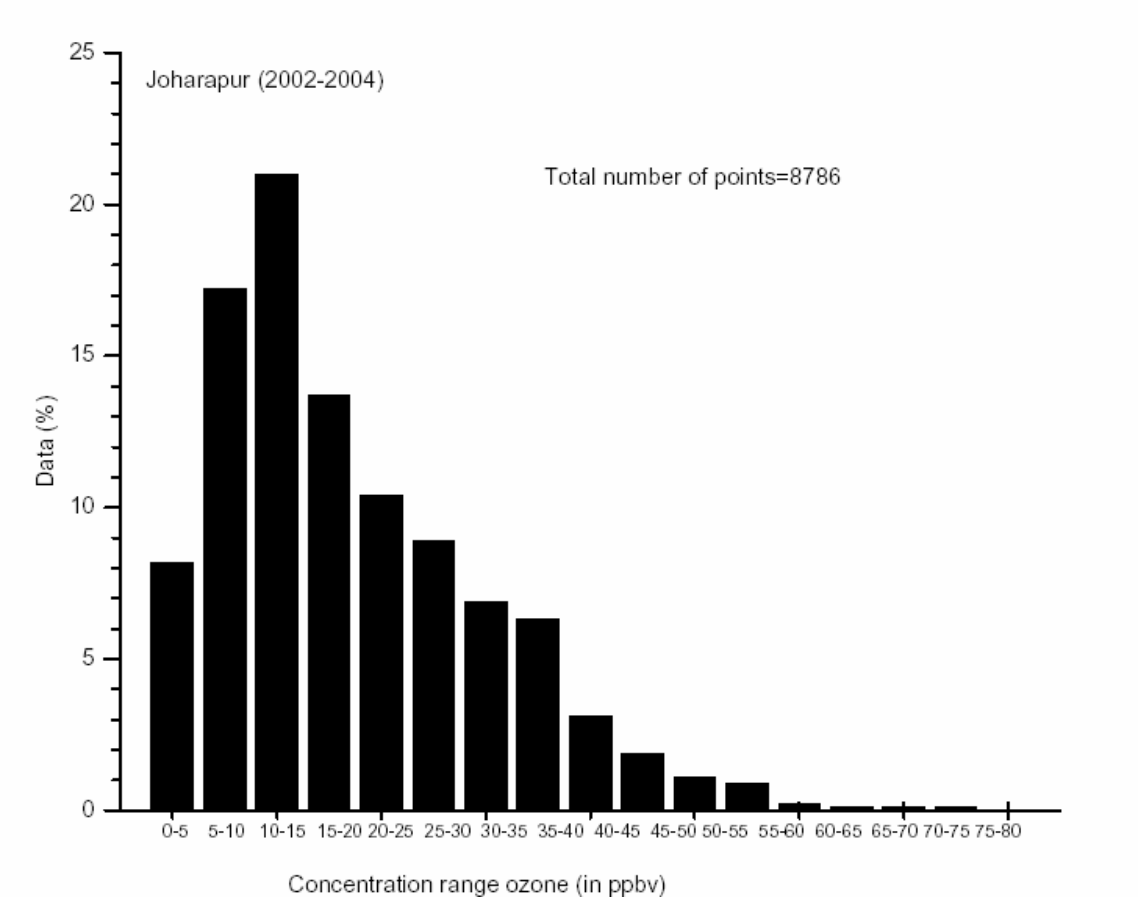

Fig. 2. Frequency distribution of ozone concentrations.

Diurnal variations

Fig. 3 shows the annual average diurnal variation of O_3 concentration in the present study period (2002-2004) at Joharapur. The vertical bars on the curve denote the 1 σ standard deviation. Diurnal variation shows maximum O_3 concentration about 29.9 ± 5.7 ppbv in the afternoon (1600 h) and minimum about 7.0 ± 3.4 ppbv in the morning (0700 h), which is related to the possible increase in the precursor-gas load of ozone due to anthropogenic activities in the rural site. The ozone concentration begins to increase just after sunrise, and attains its maximum level in the afternoon due to photochemical production of O_3 mainly from oxidation of natural and anthropogenic hydrocarbons, carbon monoxide (CO), and methane (CH_4) by hydroxyl (OH) radical in the presence of a sufficient amount of NO_x (Seinfeld and Pandis, 1998). Day-to-day

variation in O_3 is important since photochemical production of O_3 is strongly influenced by daily changing major precursor concentrations due to diversified natural and anthropogenic sources and variable influence of meteorological parameters. The low O_3 concentrations at night because of absence of photolysis of NO_2 and continuous loss of O_3 by NO_x titration. Also continuous loss of O_3 by dry and wet deposition results in minimum O_3 at the sunrise. Naja and Lal (2002) have observed the similar type of diurnal variation of O_3 at the Gadanki rural site in southeast India (13.5°N, 79.2°E, 375 m) with a maximum O_3 at 34 ppbv at noon, and a minimum at 10 ppbv in the morning. Diurnal variation of O_3 observed at Joharapur is also comparable with those observed at other urban sites in India (Khemani *et al.*, 1995; Lal *et al.*, 2000).

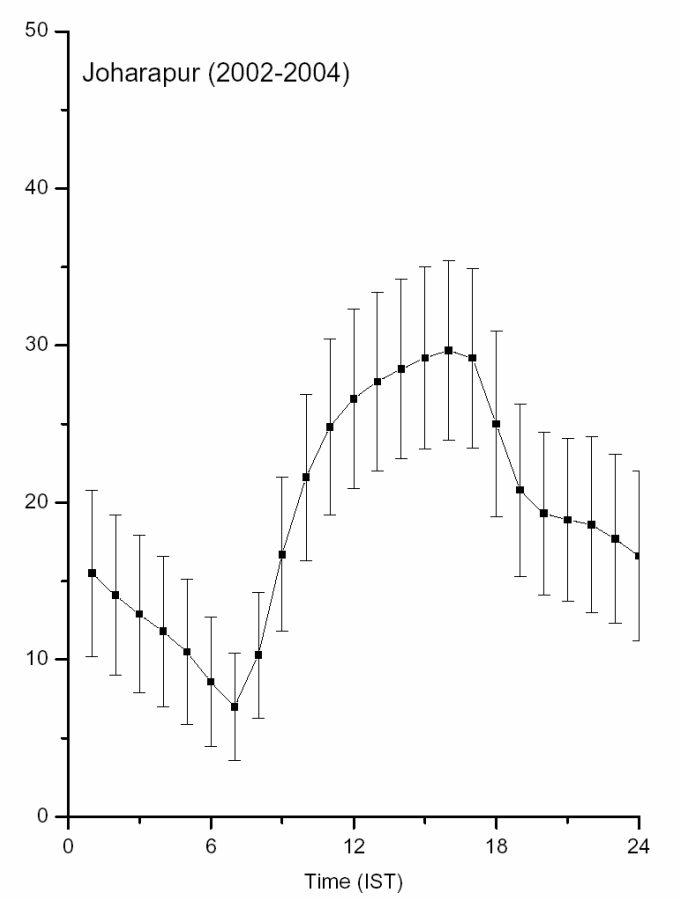

Fig. 3. Annual average diurnal profile of ozone concentrations (in ppbv). Vertical bars are 1 sigma standard deviation.

Table 1 shows monthly average O_3 concentrations and rate of change in the morning hours (0800-1100 h) and evening hours (1700-1900 h) at Joharapur for the study period. The high O_3 concentrations (31 ppbv) were in April, while low concentrations (10.8 ppbv) occurred in July, attributable to variations in precursor gases and influence of changing meteorological parameters. The morning average O_3 rate of change is higher at 4.5 ppbv/h due to fast production of O_3 by

freshly emitted precursors; whereas, in the evening it is lower at -3.3 ppbv/h because of low NO_x concentration at this site (as compare to the urban site). This is a characteristic feature of the rural environment.

Table 2 shows the average monthly variation of O_3 concentration from midnight (0000-0200 h) to midday (1200-1400 h) with 1 σ standard deviation. It shows the highest O_3 concentrations of 41.4 ± 10.4 ppbv occurring during midday in April; whereas, the lowest O_3 concentration of about 12.9 ± 2.8 occurred in July. The high O_3 in April is due to sufficient amounts of intense solar radiation along with its precursors, especially NO_x and VOC, available for more photochemical production of O_3. July rains washout O_3 precursor gases and active radical HOx ($OH + HO_2$), reflecting less photochemical activity for O_3 production. Table 2 also shows that the average rate of increase of O_3 from midnight to midday is higher (1.59 ppbv/h) in December because of longer O_3 lifetime in the winter compared to other seasons. The high rate of O_3 is also due to stagnant atmospheric conditions (temperature inversion at the ground level). The lower rate (0.27 ppbv/h) in July is due to shorter O_3 lifetimes as compared to other months, and less O_3 production (Liu *et al.*, 1987). In fact, the rate of O_3 production is slow in winter due to moderate solar intensity compare to the summer. The next highest rate of O_3 production (1.55 ppbv/h) is observed in March, which is related to the high precursor level and intense solar radiation.

Table 1. Monthly average ozone concentrations with 1 sigma standard deviation and rates of change of ozone during morning and evening hours from 2002 - 2004 at Joharapur.

Month	Average O_3 (ppbv)	1σ (ppbv)	Rate of change at (0800 - 1100 h) ppbv/h	Rate of change at (1700 - 1900 h) ppbv/h
January	24.0	2.9	6.1	-6.1
February	24.3	3.4	6.3	-5.5
March	24.6	4.6	5.8	-4.7
April	31.0	7.7	4.8	-2.8
May	21.5	6.5	3.7	-1.8
June	13.0	2.5	2.1	-1.2
July	10.8	2.3	1.7	-0.9
August	10.9	1.8	1.7	-1.0
September	14.3	3.3	3.1	-2.4
October	18.5	3,2	5.0	-4.2
November	21.2	3.7	6.0	-3.5
December	21.4	4.7	7.3	-5.4
Avg.	19.6	3.9	4.5	-3.3

Table 2. Monthly average O_3 concentrations with 1σ standard deviation observed at Joharapur during midnight (0000-0200 h) and midday (1200-1400 h) and its increase rate for 2002-2004.

Month	Midnight (0000 - 0200 h)	Midday (1200 - 1400 h)	Increase rate (ppbv/h)
January	17.7 ± 7.1	33.9 ± 5.5	1.35
February	17.4 ± 5.0	34.6 ± 5.5	1.43
March	18.2 ± 6.0	36.9 ± 6.3	1.55
April	25.2 ± 8.1	41.4 ± 10.4	1.35
May	17.8 ± 6.3	27.3 ± 8.9	0.79
June	11.4 ± 2.6	15.3 ± 4.0	0.32
July	9.7 ± 2.6	12.9 ± 2.8	0.27
August	9.8 ± 2.5	13.3 ± 2.4	0.29
September	11.8 ± 4.3	19.8 ± 4.9	0.66
October	13.7 ± 5.0	28.6 ± 5.3	1.24
November	16.8 ± 5.9	31.8 ± 5.7	1.25
December	15.9 ± 7.5	35.0 ± 6.6	1.59
Avg.	15.5 ± 5.2	27.5 ± 5.7	1.01

Average O_3 with 1σ standard deviation are shown as "avg. ± SD".

Fig. 4 shows the comparison of diurnal variations of the rate of change of O_3 (dO_3/dt) concentration (ppbv/h) in winter, premonsoon, and monsoon seasons. The highest positive rate of change of O_3 is 10.9 ppbv/h at around 0900 h and a negative rate of 9.0 ppbv/h around the 1900 h during winter, which can be attributed to the shrink in boundary layer height, as well as high precursor-gas concentration at the surface layer. The rate of change of O_3 is zero in the morning around 0700-0800 h and 1600-1700 h in the afternoon, indicating production and loss of O_3 are equal. However, net loss of O_3 observed rather late in the afternoon is due to slow NO_x titration because of low NO_x concentration. The lowest positive rate of change of O_3 is 2.4 ppbv/h and a negative rate -1.5 ppbv/h during the monsoon, which are attributable to the slow production of O_3 due to cloudy and rainy skies, which allow diffuse solar radiation at the earth's surface for photolysis of NO_2. The low dO_3/dt in monsoon is also attributed to the reduced active radicals (OH and HO_2) and precursor gases that fuel O_3 production. In the premonsoon, in spite of high air temperature, low cloud cover and low relative humidity, dO_3/dt is (7.5 ppbv/h) observed to be lower than in winter because of rapid mixing processes due to heating at the earth's surface.

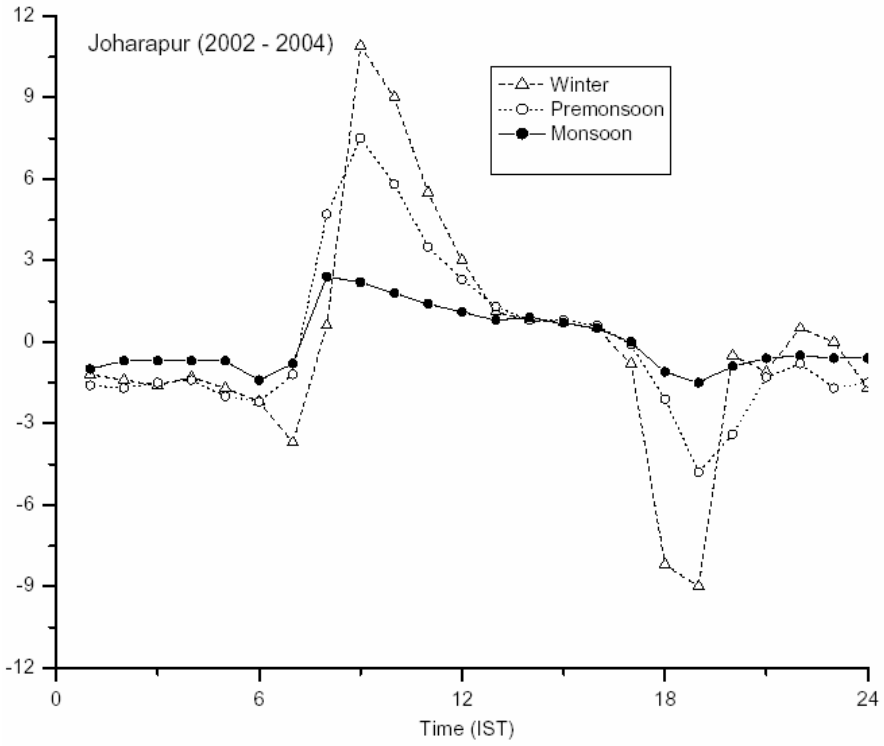

Fig. 4. A comparison of seasonal variations of average rate of change of ozone concentrations (in $ppbvh^{-1}$).

Onset time of ozone and sunrise time

Fig. 5 shows the monthly average variations of O_3 onset and sunrise times. Onset time of O_3 is defined as when O_3 starts to increase after sunrise. The figure shows that the onset time of O_3 is not fixed and that it varies from month to month on an annual cycle at this site. For example, the onset time of O_3 is minimum (45 min) in April and maximum (60 min) in July, indicating less time required to start production of O_3 after sunrise in April due to intense solar radiation and more precursor-gas concentration compared to July. The O_3 onset time suggests that high O_3 concentration during noontime is due to photochemical production of O_3.

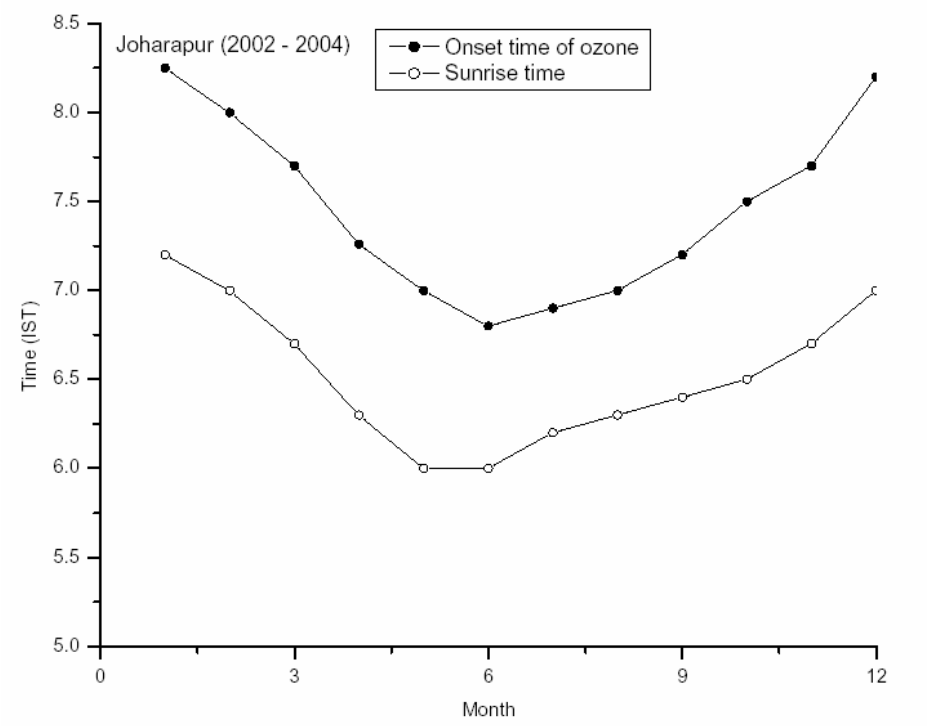

Fig. 5. Monthly mean variations of onset time of ozone and sunrise time.

Monthly variation of surface ozone in association with meteorological parameters

Fig. 6 **s**hows the average diurnal variations of O_3 concentrations in different months from December-November measured for the study period, which is related to the variation in precursor-gas concentration and to the influence of meteorological parameters. The highest maximum O_3 concentration (44.7 ± 10.8 ppbv) was observed in April due to intense solar radiation, and the lowest (15.0 ± 3.2 ppbv) was in July at 1600-1700 h. due to diffuse solar radiation available at the earth's surface. The minimum O_3 were 12.2 ± 6.1 ppbv and 4.5 ± 2.6 ppbv at about 0700 h in April and July respectively. In other months, O_3 concentration varies between the above two extreme values.

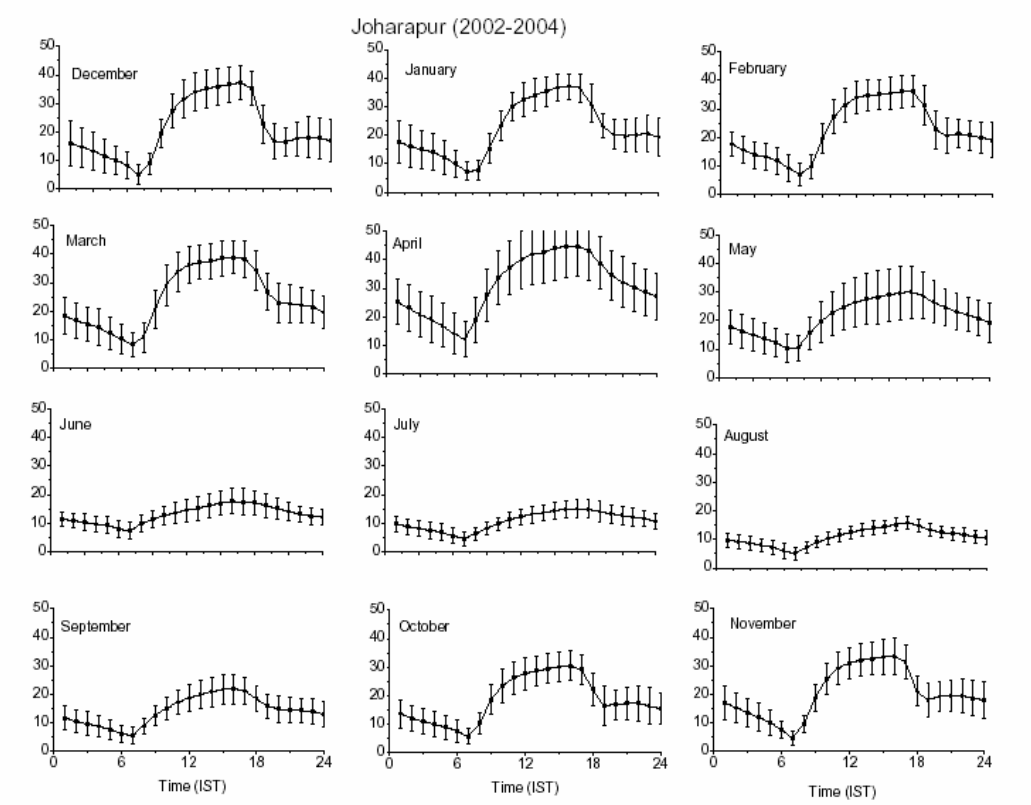

Fig. 6. Average diurnal profiles of ozone concentrations (in ppbv) measured in different months. Vertical bars are 1 sigma variations.

Table 3 summarizes average monthly variations of O_3 with air temperature, relative humidity (RH) and cloud cover for the study period. The highest O_3 of about 45 ppbv in April is due to high air temperature (40 ^oC) and more precursor concentration; whereas, the lowest of 15 ppbv in July was due to low air temperature (31^oC) and less precursor concentration. However, the average highest maximum air temperature, 42^oC, is observed in May for which the corresponding maximum O_3 observed is a low 30 ppbv. This shows a sudden decrease in O_3 concentration despite the high air temperature, indicating that other meteorological parameters, such as increased cloud cover in May, are playing equally important roles in reduced O_3 production. The lowest maximum air temperature is observed in August (28.7^oC) and January (29.9^oC), while corresponding lowest maximum O_3 is 15.8 ppbv and 37.1 ppbv, respectively. In April, the rate of natural hydrocarbon (isoprene) emissions from plants as a function of ambient air temperature (maximum at 37.5^oC) and solar radiation (Poisson *et al.*, 2000; Petron *et al.*, 2001), which is highly reactive, possibly accelerates O_3 production. Sillman and Samson (1995) observed that O_3 concentration increases with air temperature in both urban and polluted rural environments.

Table 3. Monthly average O_3 concentrations, air temperature and relative humidity with 1σ standard deviation (shown in the bracket) observed for the period 2002-2004 at Joharapur.

Month	Ozone (ppbv)			Air temperature (^oC)			Relative humidity (%)		
	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max
January	24.0 (2.9)	7.4	37.1	20.5 (3.0)	11.4	29.9	43 (9.6)	17	72
February	24.3 (3.4)	7.0	36.2	23.8 (2.8)	14.2	33.1	36 (8.8)	14	61
March	24.6 (4.6)	8.4	38.8	27.6 (2.6)	16.4	37.1	21 (7.8)	7	43
April	31.0 (7.7)	12.2	44.7	31.6 (2.5)	21.3	40.0	20 (8.7)	7	39
May	21.5 (6.5)	10.3	30.0	33.1 (1.9)	24.8	41.0	29 (10.9)	9	56
June	13.0 (2.5)	7.4	17.6	27.8 (4.1)	23.1	33.1	50 (13.4)	32	69
July	10.8 (2.3)	4.5	15.0	26.9 (3.8)	28.8	31.1	58 (10.0)	42	77
August	10.9 (1.8)	5.1	15.8	25.2 (3.4)	22.0	28.7	65 (8.9)	51	81
September	14.3 (3.3)	5.6	21.9	26.5 (1.8)	22.3	31.3	60 (10.6)	38	78
October	18.5 (3.2)	5.7	30.5	25.4 (3.1)	18.7	32.0	48 (11.6)	21	75
November	21.2 (3.7)	4.8	33.4	22.2 (2.6)	13.7	30.8	46 (7.8)	18	77
December	21.4 (4.7)	5.2	37.2	20.0 (2.4)	10.7	30.4	44 (7.4)	18	75
Avg.	19.6 (3.9)	7.0	29.9	25.9 (2.8)	18.5	33.2	43 (9.6)	23	67

Average O_3, air temperature and relative humidity with 1σ standard deviation are shown as "avg. ± SD".

Highest cloud cover (85%) is observed in August and the lowest (22%) in February for the study period. The corresponding maximum O_3 concentration observed was 16 ppbv in August and 36 ppbv in February. However, the highest maximum O_3 concentration of 45 ppbv was observed in April when cloud cover was 38%, while the lowest at 15 ppbv occurred during 83% cloud cover in July, indicating that O_3 levels not only depend on cloud cover, but on other meteorological parameters (air temperature, RH, wind speed), as well as on precursor levels. It is important to note that when cloud cover increased from 22-38% from February to April, increase in O_3 was observed from about 36 to 45 ppbv. But when cloud cover was 45% in May, O_3 abruptly reduced by 15 ppbv, indicating a sudden decrease taking place in O_3 production processes when cloud cover exceeds 38%. Tie *et al.* (2003) reported that the photolysis rate of NO_2 (J_{NO2}) decreased by 20% below cloud (overcast condition), which decreased O_3 at the surface. Jonson and Isaksen (1993) observed that clouds reduce the photochemical production of O_3 by 10-30% due to decrease in the photolysis rate of NO_2 at the ground level.

Average highest RH of 65% was observed in August and the lowest of 20% in April, and the corresponding average lowest O_3 concentration was 11 ppbv in August and the highest of 31 ppbv in April, indicating an inverse relationship of RH with O_3 concentration (Table 3). The increase in RH from 20 to 65% was observed from April to August, and corresponding O_3 decrease was observed from 31 down to 11 ppbv. Similarly, decrease in RH of 60 to 20% was

observed from September to April, and related O_3 concentration increases from 14 to 31 ppbv. Note that the highest O_3 concentration of 31 ppbv was observed in April at the time of the lowest RH of 20%. This indicates a negative impact of RH on photochemical production of O_3 in this environment. Table 4 shows seasonal variations of O_3 concentrations for the period from 2002-2004 at Joharapur.

Table 4. Seasonal variation of O_3 concentrations (ppbv) with 1σ standard deviation at Joharapur.

Year	Season	Average	Maximum	Minimum
2002	Winter	.....	.....	……
	Premonsoon	28.0 ± 6.2	30.7 ± 6.2	7.1 ± 4.1
	Monsoon	14.0 ± 3.8	20.5 ± 4.7	7.0 ± 2.9
	Postmonsoon	13.5 ± 4.8	27.0 ± 5.1	2.3 ± 1.7
2003	Winter	15.5 ± 5.0	30.0 ± 5.0	3.7 ± 2.6
	Premonsoon	27.6 ± 9.6	41.3 ± 12.2	11.0 ± 6.3
	Monsoon	10.7 ± 2.2	15.6 ± 2.6	4.5 ± 1.7
	Postmonsoon	26.3 ± 6.2	37.9 ± 6.5	7.7 ± 2.6
2004	Winter	31.0 ± 7.0	48.4 ± 6.8	9.9 ± 5.0
	Premonsoon	29.2 ± 6.4	41.8 ± 7.5	12.3 ± 5.2
	Monsoon	12.1 ± 3.6	16.4 ± 3.8	5.3 ± 3.4
	Postmonsoon	18.8 ± 4.8	31.7 ± 5.1	5.9 ± 3.4

Fig. 7 shows the average monthly variations of O_3 for the period 2002-2004 at Joharapur, indicating that year-to-year (temporal) variation is important. The O_3 shows a distinct variation—hourly average maximum O_3 at noon is 88 ppbv in April, 2003 exceeds the 80 ppbv air-quality standard (curve A). However, corresponding O_3 values are 48 ppbv and 62 ppbv in April 2002 and 2004, respectively. Average daily hourly O_3 maxima for the month is highest at about 60 ppbv in April 2003, and next highest at 52 ppbv in January 2004, with the lowest at 34 ppbv in March 2002 (curve B). Similarly, the average of all hourly O_3 values for the month show the highest 39 ppbv in April 2003, 34 ppbv in April 2004, and 20 ppbv in May 2002 (curve C). The lowest of the daily hourly O_3 maxima for the month is 32 ppbv in April 2003, 24 ppbv in April 2004, and 17 ppbv in May 2002 (curve D). This indicates that highest O_3 levels were observed in April 2003 followed by April 2004, suggesting not only year-to–year, but day–to-day (hourly average) variations are more important in the study of air pollution.

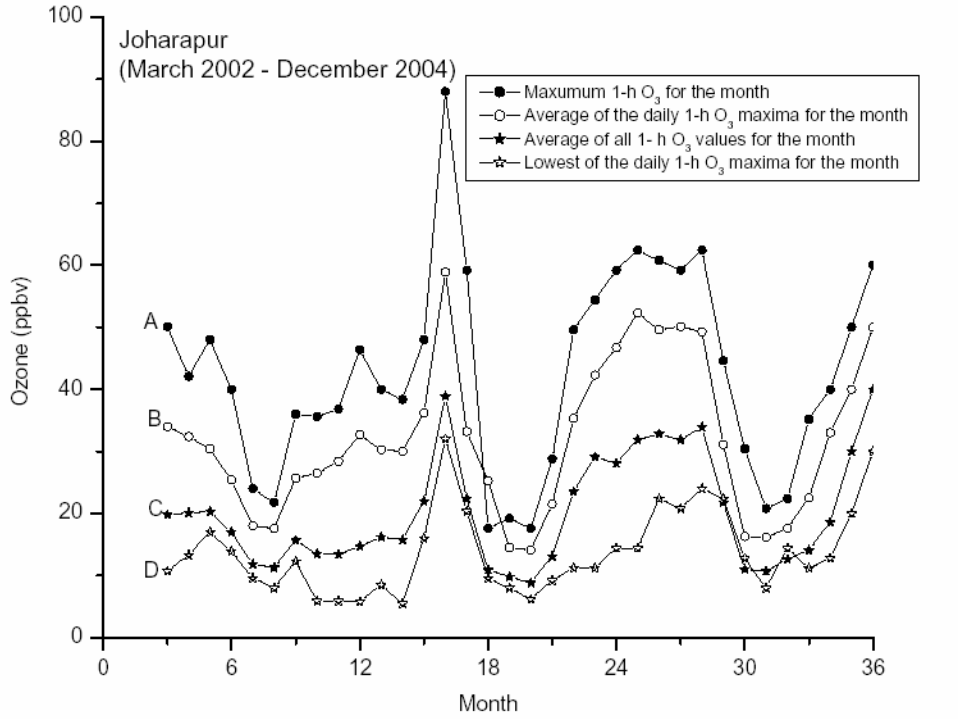

Fig. 7. Temporal variations of ozone concentrations.

Fig. 8 shows the average diurnal variation of O_3 concentrations in different seasons. The highest maximum O_3 of about 38.5 ± 5.7 ppbv at 1600 h and lowest 17.4 ± 3.7 ppbv at 1700 h in winter and monsoon, respectively. Corresponding lowest minimums are 6.8 ± 3.8 ppbv and 5.6 ± 2.6 ppbv at 0700 h. The highest O_3 in winter is attributed to a low mixing height which results in the trapping of pollutants near the earth's surface due to temperature inversion (Oke, 1978). The premonsoon season also shows the highest maximum ozone value 37.7 ± 8.7 ppbv at around 1500 h, and the lowest minimum 10.4 ± 4.9 ppbv at about 0700 h; similar to winter season because of high air temperature, low cloud cover, low RH, and no rainfall activity. Such diurnal variation is typically observed in urban areas in India and is a consequence of the photochemical production and NO_x titration under substantial amounts of NO_x concentration. The similar diurnal magnitude of O_3 concentration is observed at the rural Joharapur site which indicates that sufficient NO_x load is present in the rural environment because of increasing human activity, such as transport and biomass burning. However, peak O_3 concentration (hump on the curves) will be attained generally in the afternoon in the rural site because of less NO_x titration. Liu *et al.* (1987) reported that production efficiency of O_3 (ozone produced per unit NO_x loss) is more at the rural site than in the city, since the NO_x level is relatively lower, which possibly enhances O_3 concentration after noon at Joharapur. In rural India, the burning of biofuels (Venkataraman *et al.*, 2005), such as wood, dung, biomass burning and agricultural waste, is a major source of pollutants throughout the year. These are O_3 precursors (Lelieveld *et al.*, 2001). The NO_x

contributions from the above sources are more during premonsoon, amounting to 19% of the total NO_x emission (Galanter *et al.*, 2000; Gerg *et al.*, 2001) which increases O_3 in the April.

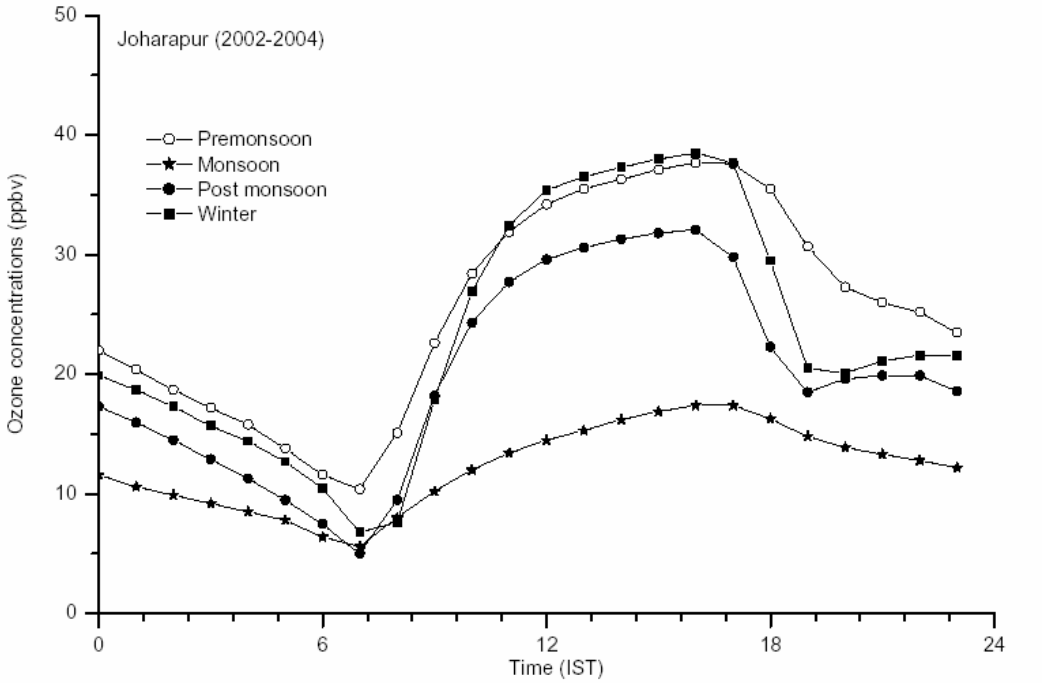

Fig. 8. Seasonal diurnal variations of average ozone concentrations.

In the year 1965-1966 only 0.6 of a million tons (1 ton = 1000 kg) of fertilizer was used in India, whereas use had increased to 18.7 million ton by 1999-2000 (India, 2002). That's an increase rate of 0.5 million ton/yr from 1965 through 2000. The emission of NO_x due to increase use of fertilizer is estimated to be 0.11 Tg N/yr in India (Yienger and Levy, 1995). Increasing fertilizer use emits more NO_x, which possibly enhances O_3 in the rural areas during summer.

Fig. 9 (a-f) shows the mean monthly variations of maximum O_3 concentrations along with meteorological parameters. Higher O_3 (44.7 ± 10.8 ppbv) is observed in April and lower (15.0 ± 3.2 ppbv) in July with 1 σ standard deviation (Fig. 9a). However, highest air temperature of 41.0°C is observed in May and the lowest at 28.7°C in August (Fig. 9b). The highest relative humidity of 81% is observed in August and the lowest of 39% in April (Fig. 9c). The increase in O_3 concentrations in April is attributed to possible increase in O_3 precursor levels and favorable influence of meteorological parameters. The emission of isoprene (VOC) from plants is a function of ambient air temperature. Biomass burning in April is heaviest when mostly clear sky conditions are common, which influences O_3 production (Crutzen and Andreae, 1990). The highest rainfall (184 mm) is recorded in September with no rainfall December through April (Fig. 9d). An abrupt decrease in O_3 by 15 ppbv is observed from April to May due to increased cloud cover from 38-45% (Fig. 9e) and RH 39-56%; while air temperature increases from 40-41°C.

This indicates that O_3 decreases when cloud cover and RH increase, despite increased air temperature. Wind speed was about 4.5 m/s with a southwesterly direction during monsoon season and northeasterly of 1 m/s in winter and premonsoon seasons (Fig. 9f).

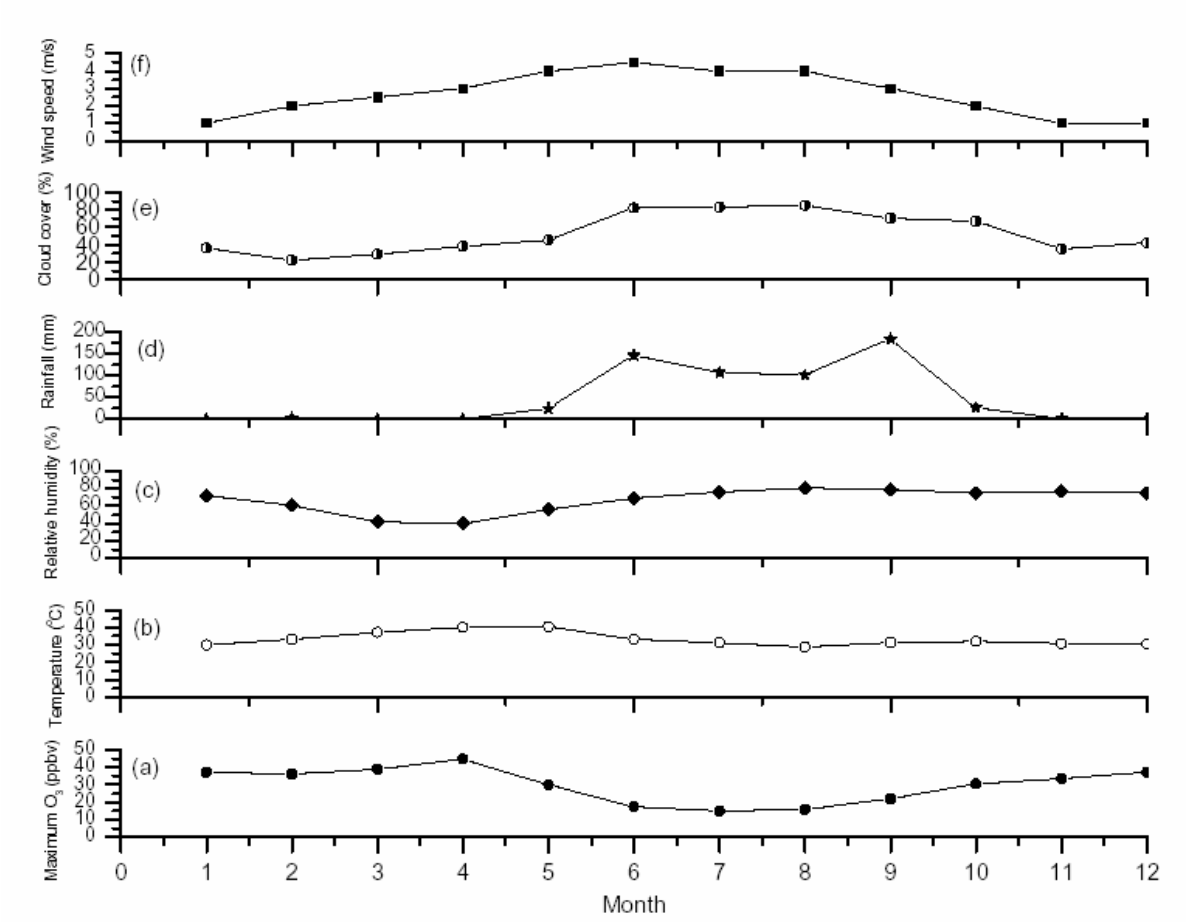

Fig. 9. Average monthly variation of maximum ozone (a), maximum air temperature (b), relative humidity (c), rainfall (d), cloud cover (e), and wind speed (f) for the period 2002-2004 measured at Joharapur.

Fig. 10 (a-d) shows variations of maximum O_3 concentrations versus maximum air temperature, RH, cloud cover and wind speed (scattered diagram) recorded at Joharapur. It shows that air temperature is positively related with O_3, whereas RH, cloud cover and wind speed are negatively related. It is important to note that the coefficient of correlation (R) of temperature with O_3 is 0.34, which is not as rich as expected; suggesting maximum O_3 not only depends on temperature, but more on other meteorological parameters like cloud cover, RH and wind speed, and mostly on major precursor concentrations. The cloud cover (R = -0.66) and RH (R = -0.64) possess a good negative relationship with O_3, which plays an important role in building up O_3

concentration, whereas wind speed (R = -0.26) shows poor negative relationship with O_3 concentration.

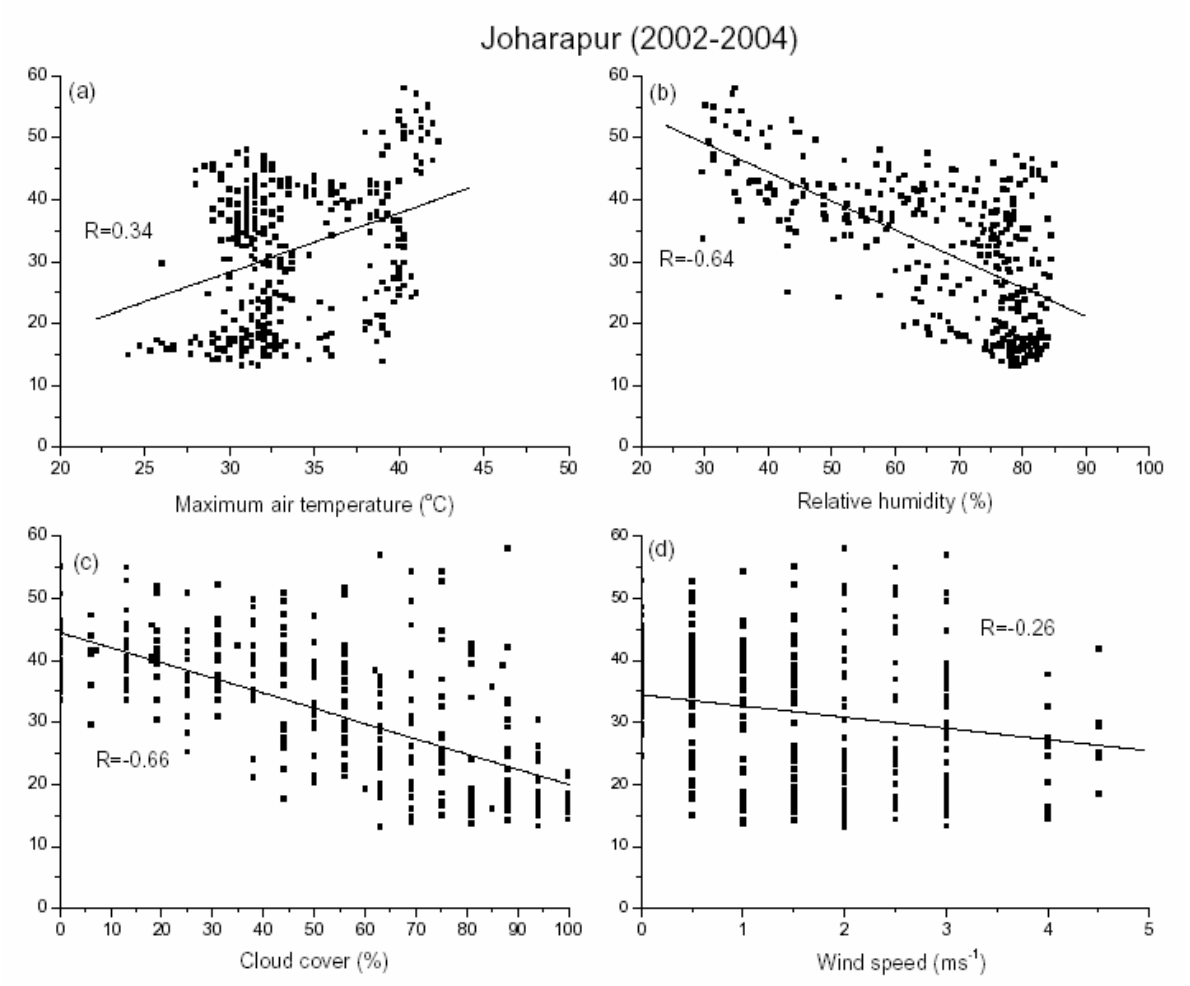

Fig. 10. The variation of all hourly maximum ozone concentrations (in ppbv) (scattered diagram) versus maximum air temperature (a), relative humidity (b), cloud cover (c), and wind speed (d).

Comparison of rate of change of surface ozone

Table 5 shows a comparison of rate of change of O_3 at Joharapur and observations at different sites in India. The annual average rates of change of O_3 during the evening hours (1700-1900 h) at Joharapur is estimated to be -3.3 ppbv/h, which is higher than the rural site Gadanki (-2.6 ppbv/h) (13.5°N, 79.2°E, 375 m), indicating Joharapur is more polluted than Gadanki. The rates of change of O_3 during the morning (0800-1100 h) are 4.5 and 4.8 ppbv/h at Joharapur and Gadanki, respectively. The rates of change of O_3 during the evening hours at urban sites Delhi (28.6°N, 77.2°E, 216 m) and Ahmedabad (23°N, 72.6°E, 49 m) in India are higher to their respective rates during the morning hours (Table 5), which are attributed to the higher NOx

concentration from commuter vehicular emission, responsible for fast titration of O_3 in the evening (Naja and Lal, 2002). Thumba (8.6°N, 77°E, 2 m) a coastal site shows a morning rate of O_3 production higher, while evening rate is low compared to Joharapur.

Table 5. Comparison of observed rate of change of O_3 concentrations at different sites in India.

Site	Rate of change at0800 - 1100 h (ppbv/h)	Rate of change at 1700 - 1900 h (ppbv/h)
Joharapur	4.5	-3.3
Gadanki	4.6	-2.6
Delhi	4.5	-5.3
Ahmedabad	5.9	-6.4
Tranquebar	3.1	-2.8
Thumba	5.5	-1.4

Comparison of monthly variation of surface ozone with other sites in India

Fig. 11 shows a comparison of monthly variations of maximum O_3 concentrations observed at Joharapur with rural site Gadanki (Naja and Lal, 2002), and urban sites Pune (18.5°N, 73.9°E, 559 m) and Ahmedabad (Khemani, *et al.*, 1995; Lal *et al.*, 2000) in India. In general, it shows a similar pattern of monthly variation in O_3 at all sites; however, there are differences in O_3 concentration due to shifts in season from one site to another. The O_3 at Joharapur shows smaller monthly amplitude (highest-lowest) variation (20 ppbv) when compared with Gadanki (25 ppbv) and Ahmedabad (35 ppbv). All four sites exhibit low O_3 during the southwest monsoon, while Gadanki extends into October due to northeast monsoon rain. The highest O_3 occurs in April at Joharapur due to intense solar radiation with a possible increase in precursors, which accelerate production of O_3 by photooxidation processes. The highest O_3 at Gadanki was observed in March. The low O_3 during monsoon at Joharapur is attributed to the low precursor concentrations and cloudy sky.

Average highest maximum O_3 in April at Joharapur is low (about 45 ppbv) compared to many global sites, such as the northern United States and China, where O_3 concentrations exceeding 80 ppbv for many days have been commonly observed (Aneja *et al.,* 1999; Luo *et al.*, 2000). However, there are few instances of peak O_3 concentration in April which exceeds 70-80 ppbv at Joharapur.

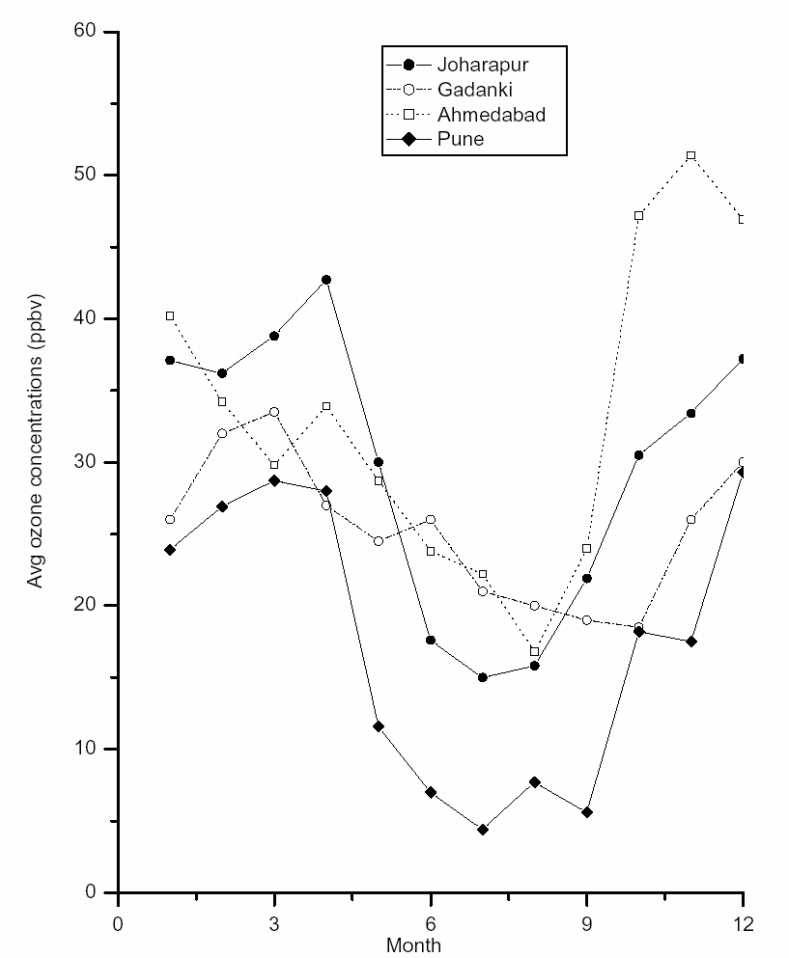

Fig. 11. A comparison of monthly average ozone concentrations measured at Joharapur (rural site) with those at other sites in India, Pune (urban site) (1991-1992), Gadanki (rural site) (1993-1996) and Ahamedabad (urban site) (1991-1995) values are averaged concentrations through out all study period.

CONCLUSIONS

The results of O_3 measurements and meteorological parameters at Joharapur have shown that O_3 concentration varies with chemical parameters and meteorological conditions. The air temperature is positively, but poorly, related with O_3, whereas cloud cover and relative humidity are negatively, but strongly, related. The wind speeds show poor negative relationship with O_3 concentration. The highest maximum O_3 concentration observed in April due to photochemical production in the rural environment of Joharapur is more or less similar to urban sites in India. This is possibly due to the significant increase of major precursor load in the rural environment to support O_3 production involving complex and nonlinear photochemical chain reactions. There is a need for more extensive measurements of O_3 and precursor gases, especially NO_x and

hydrocarbons, at different sites, and for modeling studies to understand the various processes controlling variability of ozone level all over the Indian region.

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