

## **Measurements of Surface Ozone in Rural Site of India**

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### **Abstract**

It is known that the formation of surface ozone (O<sub>3</sub>) is chemically linked to the emissions of major precursor gases, nitrogen oxides (NO<sub>x</sub>) 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<sub>3</sub> formation in a rural site. For this purpose, measurements of O<sub>3</sub> and selected meteorological parameters have been made at Johrapur (19.3° N, 75.2° E, 474 m above sea level), a tropical rural site in India since March 2002. The annual average diurnal variation of O<sub>3</sub> shows that maximum O<sub>3</sub> concentration is  $29.9 \pm 5.7$  ppbv at noon and minimum  $7.0 \pm 3.4$  ppbv in the morning with 1  $\sigma$  standard deviation. The monthly average high (low) O<sub>3</sub>  $44.7 \pm 10.8$  ppbv ( $15.0 \pm 3.2$  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<sub>3</sub> concentration has been observed as a function of season, which shows that the seasonal highest O<sub>3</sub> concentration is  $37.7 \pm 8.7$  ppbv at noon in premonsoon and lowest  $17.4 \pm 3.7$  ppbv in monsoon season. The hourly averaged O<sub>3</sub> 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<sub>x</sub> 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 19<sup>th</sup> 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  $\text{NO}_x$  concentration is responsible for increasing  $\text{O}_3$  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  $\text{O}_3$  production factors necessitates measurements at rural sites.

A few scattered  $\text{O}_3$  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  $\text{O}_3$  at a rural site except at Gadanki, which is located in southeast India about 800 km away from the present  $\text{O}_3$  measurement site. In this paper, we present  $\text{O}_3$  measurements which have been carried out for the first time in this region at Johrapur, a rural site in western India. Diurnal and seasonal variability in  $\text{O}_3$  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 Johrapur is located in western India. Johrapur's population was less than 2,500 in 2001 (Fig. 1). The industrial city Mumbai ( $19.1^\circ\text{N}$ ,  $72.9^\circ\text{E}$ , 11 m) is about 300 km to the west and Aurangabad ( $19.9^\circ\text{N}$ ,  $75.3^\circ\text{E}$ , 581 m) is 80 km northeast of Johrapur. Both contribute to the enhancement of  $\text{O}_3$  precursor gases in these areas. The most prominent meteorological feature at Johrapur 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  $\text{O}_3$ . 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  $42^\circ\text{C}$  at noon and minimum  $20^\circ\text{C}$  in the morning.

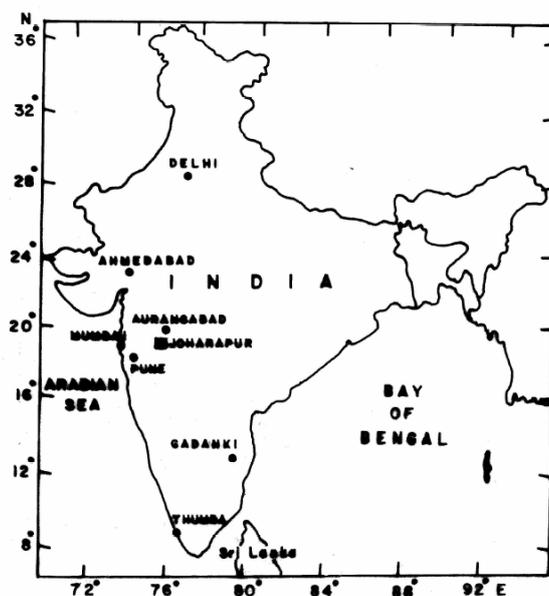


Fig. 1. Location map of the rural site Joharapur, India.

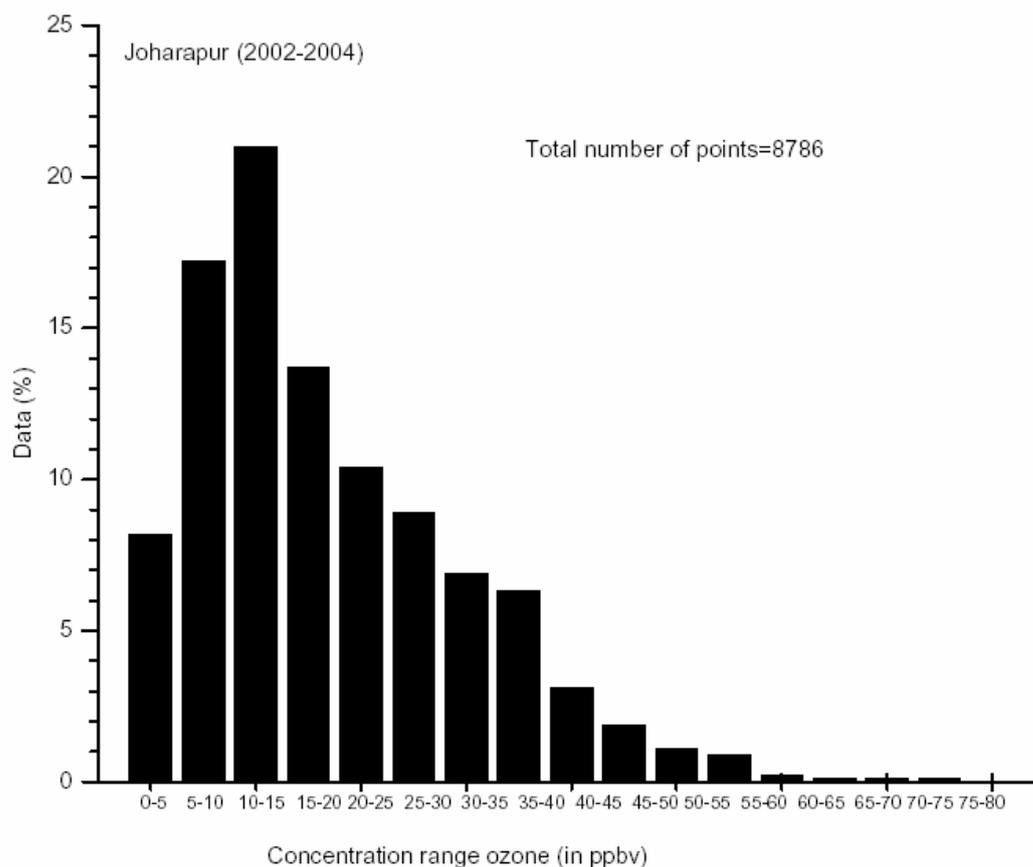
### *Measurement techniques*

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<sub>3</sub> exceeds air quality standards at noon on few occasions in the premonsoon (hot) season in 2003. The results of the diurnal variation of O<sub>3</sub> and variations in different seasons are presented and discussed below.

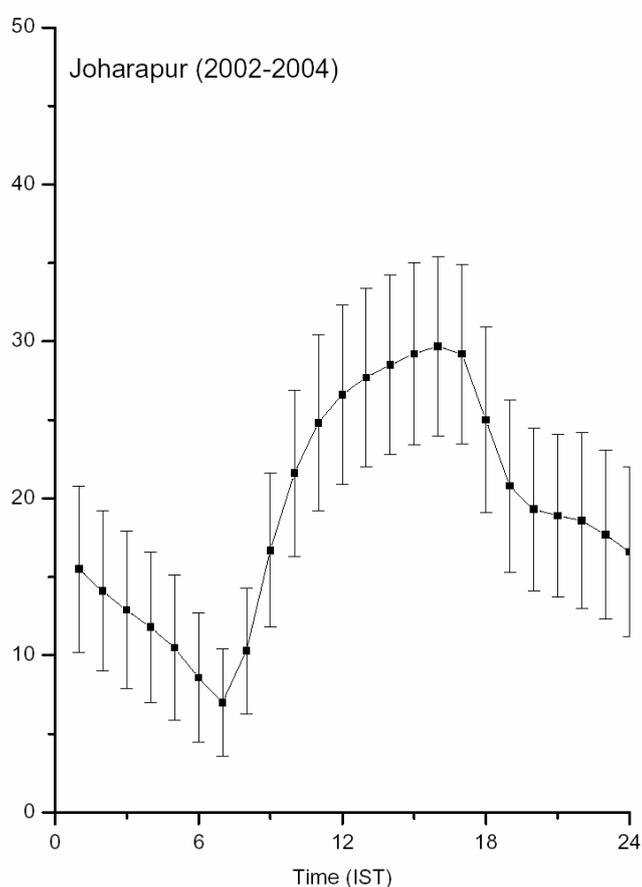


**Fig. 2.** Frequency distribution of ozone concentrations.

### ***Diurnal variations***

Fig. 3 shows the annual average diurnal variation of O<sub>3</sub> concentration in the present study period (2002-2004) at Joharapur. The vertical bars on the curve denote the 1  $\sigma$  standard deviation. Diurnal variation shows maximum O<sub>3</sub> concentration about  $29.9 \pm 5.7$  ppbv in the afternoon (1600 h) and minimum about  $7.0 \pm 3.4$  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<sub>3</sub> mainly from oxidation of natural and anthropogenic hydrocarbons, carbon monoxide (CO), and methane (CH<sub>4</sub>) by hydroxyl (OH) radical in the presence of a sufficient amount of NO<sub>x</sub> (Seinfeld and Pandis, 1998). Day-to-day

variation in O<sub>3</sub> is important since photochemical production of O<sub>3</sub> 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<sub>3</sub> concentrations at night because of absence of photolysis of NO<sub>2</sub> and continuous loss of O<sub>3</sub> by NO<sub>x</sub> titration. Also continuous loss of O<sub>3</sub> by dry and wet deposition results in minimum O<sub>3</sub> at the sunrise. Naja and Lal (2002) have observed the similar type of diurnal variation of O<sub>3</sub> at the Gadanki rural site in southeast India (13.5°N, 79.2°E, 375 m) with a maximum O<sub>3</sub> at 34 ppbv at noon, and a minimum at 10 ppbv in the morning. Diurnal variation of O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> rate of change is higher at 4.5 ppbv/h due to fast production of O<sub>3</sub> by

freshly emitted precursors; whereas, in the evening it is lower at -3.3 ppbv/h because of low NO<sub>x</sub> 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<sub>3</sub> concentration from midnight (0000-0200 h) to midday (1200-1400 h) with 1 σ standard deviation. It shows the highest O<sub>3</sub> concentrations of 41.4 ± 10.4 ppbv occurring during midday in April; whereas, the lowest O<sub>3</sub> concentration of about 12.9 ± 2.8 occurred in July. The high O<sub>3</sub> in April is due to sufficient amounts of intense solar radiation along with its precursors, especially NO<sub>x</sub> and VOC, available for more photochemical production of O<sub>3</sub>. July rains washout O<sub>3</sub> precursor gases and active radical HO<sub>x</sub> (OH + HO<sub>2</sub>), reflecting less photochemical activity for O<sub>3</sub> production. Table 2 also shows that the average rate of increase of O<sub>3</sub> from midnight to midday is higher (1.59 ppbv/h) in December because of longer O<sub>3</sub> lifetime in the winter compared to other seasons. The high rate of O<sub>3</sub> 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<sub>3</sub> lifetimes as compared to other months, and less O<sub>3</sub> production (Liu *et al.*, 1987). In fact, the rate of O<sub>3</sub> production is slow in winter due to moderate solar intensity compare to the summer. The next highest rate of O<sub>3</sub> 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.

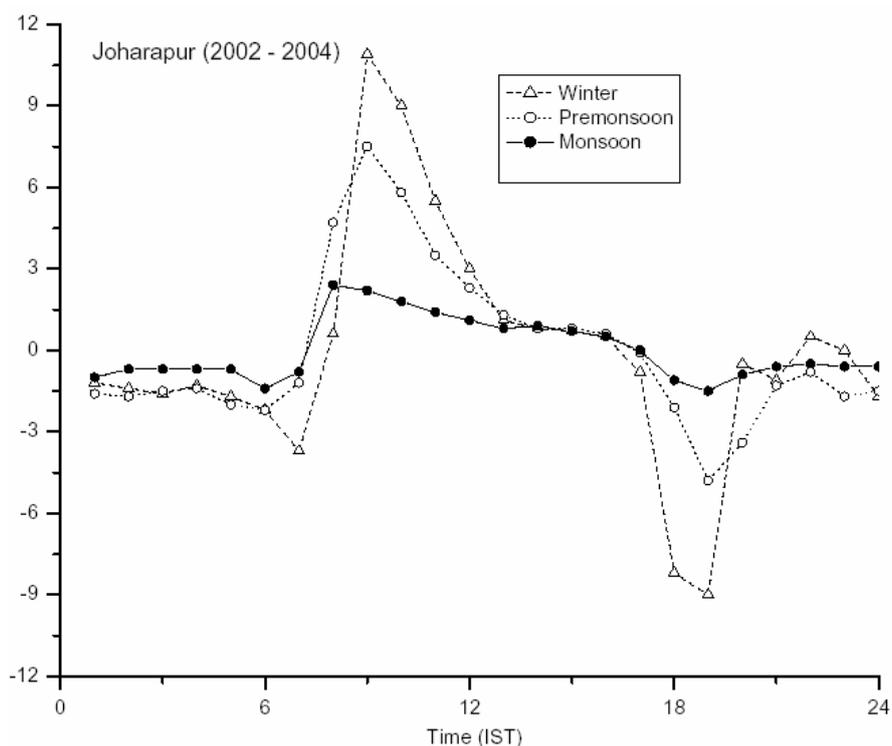
Month	Average O <sub>3</sub> (ppbv)	1σ (ppbv)	Rate of change at (0800 - 1100 h) ppbv/h	Rate of change at (1700 - 1900 h) ppbv/h
January	24.0	2.9	6.1	-6.1
February	24.3	3.4	6.3	-5.5
March	24.6	4.6	5.8	-4.7
April	31.0	7.7	4.8	-2.8
May	21.5	6.5	3.7	-1.8
June	13.0	2.5	2.1	-1.2
July	10.8	2.3	1.7	-0.9
August	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<sub>3</sub> concentrations with 1σ standard deviation observed at Johrapur 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<sub>3</sub> with 1σ standard deviation are shown as “avg. ± SD”.

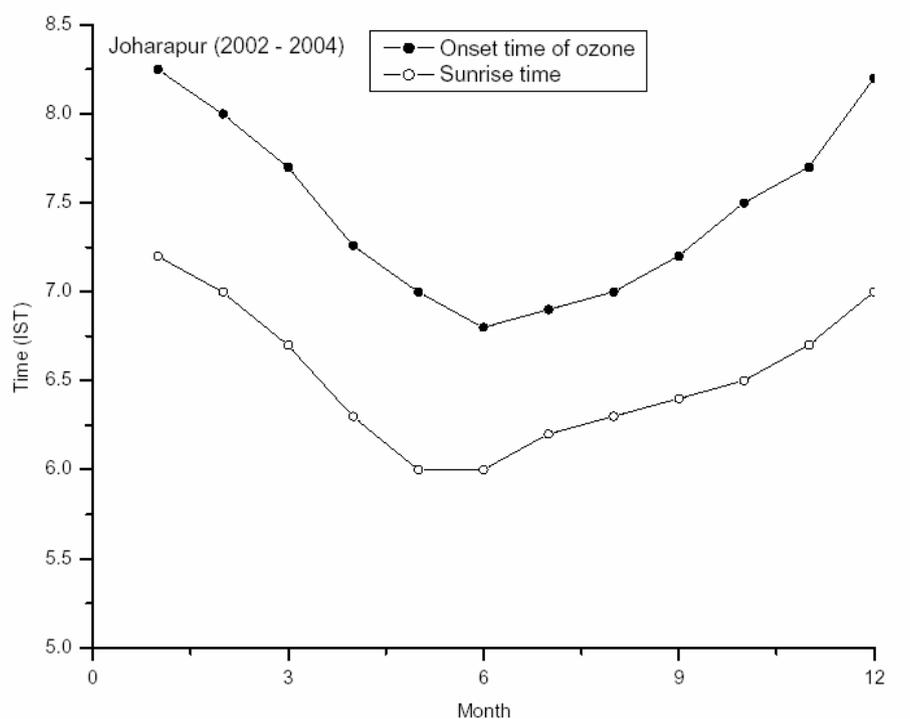
Fig. 4 shows the comparison of diurnal variations of the rate of change of O<sub>3</sub> (dO<sub>3</sub>/dt) concentration (ppbv/h) in winter, premonsoon, and monsoon seasons. The highest positive rate of change of O<sub>3</sub> is 10.9 ppbv/h at around 0900 h and a negative rate of 9.0 ppbv/h around 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<sub>3</sub> is zero in the morning around 0700-0800 h and 1600-1700 h in the afternoon, indicating production and loss of O<sub>3</sub> are equal. However, net loss of O<sub>3</sub> observed rather late in the afternoon is due to slow NO<sub>x</sub> titration because of low NO<sub>x</sub> concentration. The lowest positive rate of change of O<sub>3</sub> 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<sub>3</sub> due to cloudy and rainy skies, which allow diffuse solar radiation at the earth's surface for photolysis of NO<sub>2</sub>. The low dO<sub>3</sub>/dt in monsoon is also attributed to the reduced active radicals (OH and HO<sub>2</sub>) and precursor gases that fuel O<sub>3</sub> production. In the premonsoon, in spite of high air temperature, low cloud cover and low relative humidity, dO<sub>3</sub>/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 ppbv h<sup>-1</sup>).

***Onset time of ozone and sunrise time***

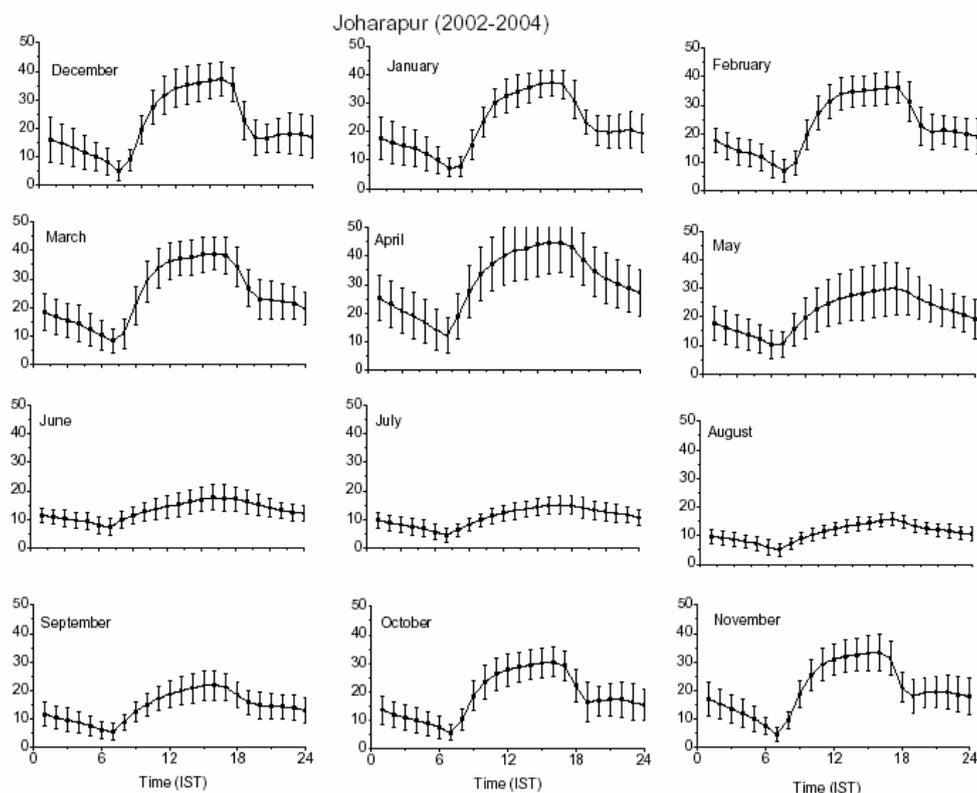
Fig. 5 shows the monthly average variations of O<sub>3</sub> onset and sunrise times. Onset time of O<sub>3</sub> is defined as when O<sub>3</sub> starts to increase after sunrise. The figure shows that the onset time of O<sub>3</sub> is not fixed and that it varies from month to month on an annual cycle at this site. For example, the onset time of O<sub>3</sub> is minimum (45 min) in April and maximum (60 min) in July, indicating less time required to start production of O<sub>3</sub> after sunrise in April due to intense solar radiation and more precursor-gas concentration compared to July. The O<sub>3</sub> onset time suggests that high O<sub>3</sub> concentration during noontime is due to photochemical production of O<sub>3</sub>.



**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 shows the average diurnal variations of O<sub>3</sub> 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<sub>3</sub> concentration ( $44.7 \pm 10.8$  ppbv) was observed in April due to intense solar radiation, and the lowest ( $15.0 \pm 3.2$  ppbv) was in July at 1600-1700 h. due to diffuse solar radiation available at the earth's surface. The minimum O<sub>3</sub> were  $12.2 \pm 6.1$  ppbv and  $4.5 \pm 2.6$  ppbv at about 0700 h in April and July respectively. In other months, O<sub>3</sub> 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 ( $40^\circ C$ ) and more precursor concentration; whereas, the lowest of 15 ppbv in July was due to low air temperature ( $31^\circ C$ ) and less precursor concentration. However, the average highest maximum air temperature,  $42^\circ C$ , 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 ( $28.7^\circ C$ ) and January ( $29.9^\circ C$ ), 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  $37.5^\circ C$ ) 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<sub>3</sub> 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 (°C)			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<sub>3</sub>, 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<sub>3</sub> concentration observed was 16 ppbv in August and 36 ppbv in February. However, the highest maximum O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> was observed from about 36 to 45 ppbv. But when cloud cover was 45% in May, O<sub>3</sub> abruptly reduced by 15 ppbv, indicating a sudden decrease taking place in O<sub>3</sub> production processes when cloud cover exceeds 38%. Tie *et al.* (2003) reported that the photolysis rate of NO<sub>2</sub> (J<sub>NO2</sub>) decreased by 20% below cloud (overcast condition), which decreased O<sub>3</sub> at the surface. Jonson and Isaksen (1993) observed that clouds reduce the photochemical production of O<sub>3</sub> by 10-30% due to decrease in the photolysis rate of NO<sub>2</sub> at the ground level.

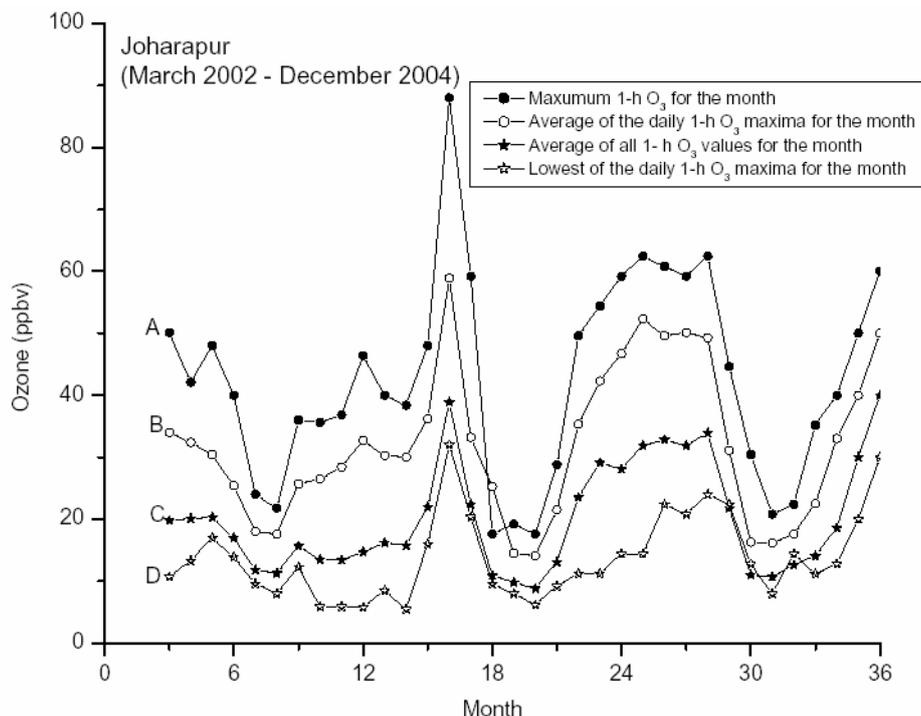
Average highest RH of 65% was observed in August and the lowest of 20% in April, and the corresponding average lowest O<sub>3</sub> concentration was 11 ppbv in August and the highest of 31 ppbv in April, indicating an inverse relationship of RH with O<sub>3</sub> concentration (Table 3). The increase in RH from 20 to 65% was observed from April to August, and corresponding O<sub>3</sub> 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<sub>3</sub> concentration increases from 14 to 31 ppbv. Note that the highest O<sub>3</sub> 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<sub>3</sub> in this environment. Table 4 shows seasonal variations of O<sub>3</sub> concentrations for the period from 2002-2004 at Joharapur.

**Table 4.** Seasonal variation of O<sub>3</sub> 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

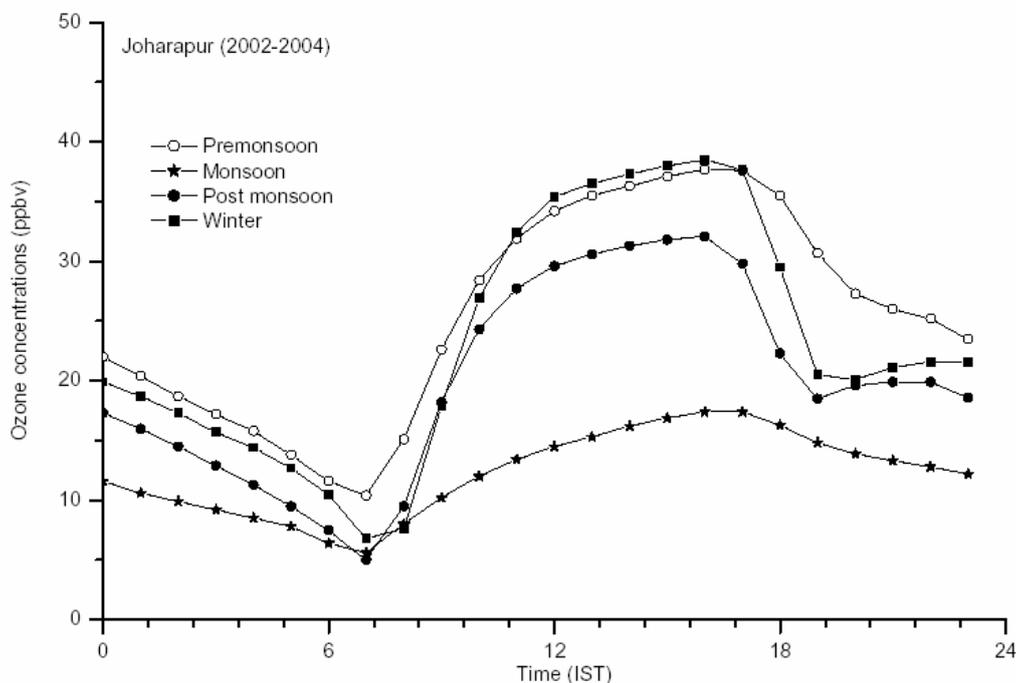
Fig. 7 shows the average monthly variations of O<sub>3</sub> for the period 2002-2004 at Joharapur, indicating that year-to-year (temporal) variation is important. The O<sub>3</sub> shows a distinct variation—hourly average maximum O<sub>3</sub> at noon is 88 ppbv in April, 2003 exceeds the 80 ppbv air-quality standard (curve A). However, corresponding O<sub>3</sub> values are 48 ppbv and 62 ppbv in April 2002 and 2004, respectively. Average daily hourly O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> concentrations in different seasons. The highest maximum O<sub>3</sub> of about  $38.5 \pm 5.7$  ppbv at 1600 h and lowest  $17.4 \pm 3.7$  ppbv at 1700 h in winter and monsoon, respectively. Corresponding lowest minimums are  $6.8 \pm 3.8$  ppbv and  $5.6 \pm 2.6$  ppbv at 0700 h. The highest O<sub>3</sub> 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  $37.7 \pm 8.7$  ppbv at around 1500 h, and the lowest minimum  $10.4 \pm 4.9$  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<sub>x</sub> titration under substantial amounts of NO<sub>x</sub> concentration. The similar diurnal magnitude of O<sub>3</sub> concentration is observed at the rural Joharapur site which indicates that sufficient NO<sub>x</sub> load is present in the rural environment because of increasing human activity, such as transport and biomass burning. However, peak O<sub>3</sub> concentration (hump on the curves) will be attained generally in the afternoon in the rural site because of less NO<sub>x</sub> titration. Liu *et al.* (1987) reported that production efficiency of O<sub>3</sub> (ozone produced per unit NO<sub>x</sub> loss) is more at the rural site than in the city, since the NO<sub>x</sub> level is relatively lower, which possibly enhances O<sub>3</sub> 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<sub>3</sub> precursors (Lelieveld *et al.*, 2001). The NO<sub>x</sub>

contributions from the above sources are more during premonsoon, amounting to 19% of the total NO<sub>x</sub> emission (Galanter *et al.*, 2000; Gerg *et al.*, 2001) which increases O<sub>3</sub> in the April.

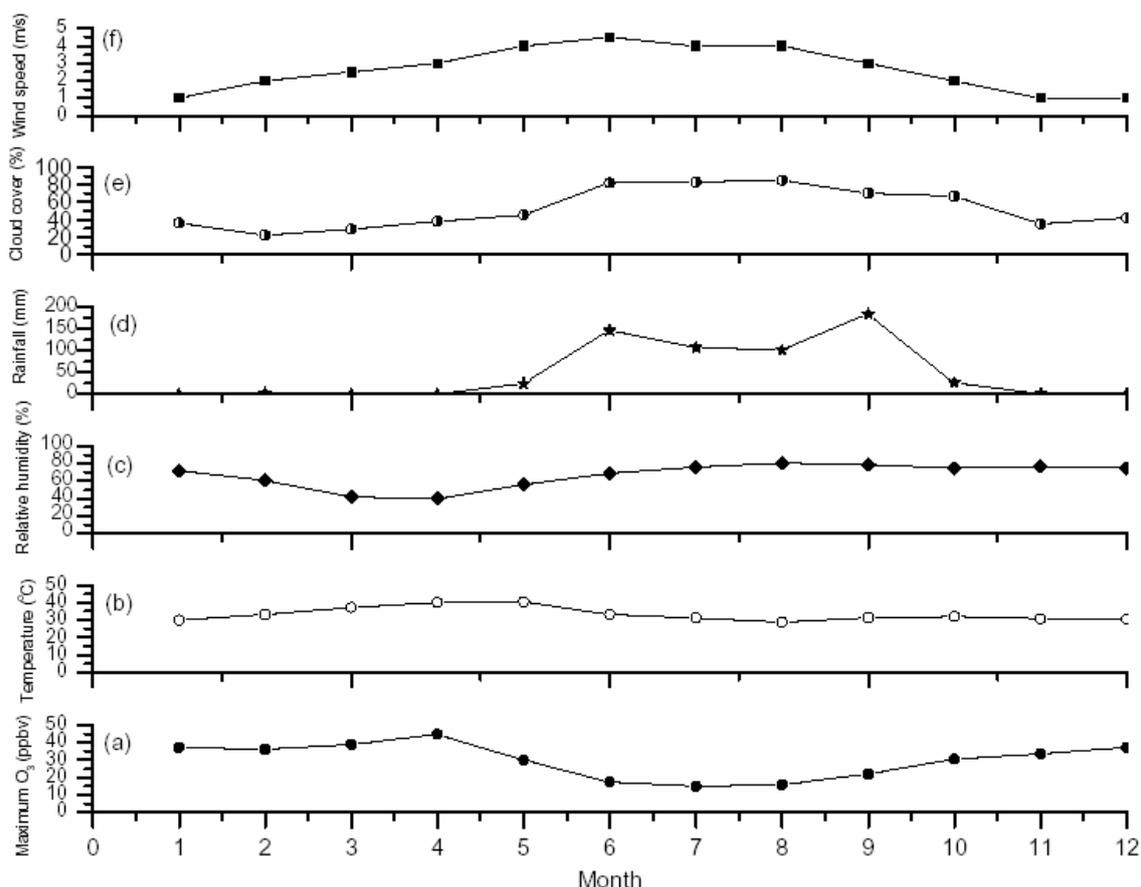


**Fig. 8.** Seasonal diurnal variations of average ozone concentrations.

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<sub>x</sub> 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<sub>x</sub>, which possibly enhances O<sub>3</sub> in the rural areas during summer.

Fig. 9 (a-f) shows the mean monthly variations of maximum O<sub>3</sub> concentrations along with meteorological parameters. Higher O<sub>3</sub> ( $44.7 \pm 10.8$  ppbv) is observed in April and lower ( $15.0 \pm 3.2$  ppbv) in July with 1  $\sigma$  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<sub>3</sub> concentrations in April is attributed to possible increase in O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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.

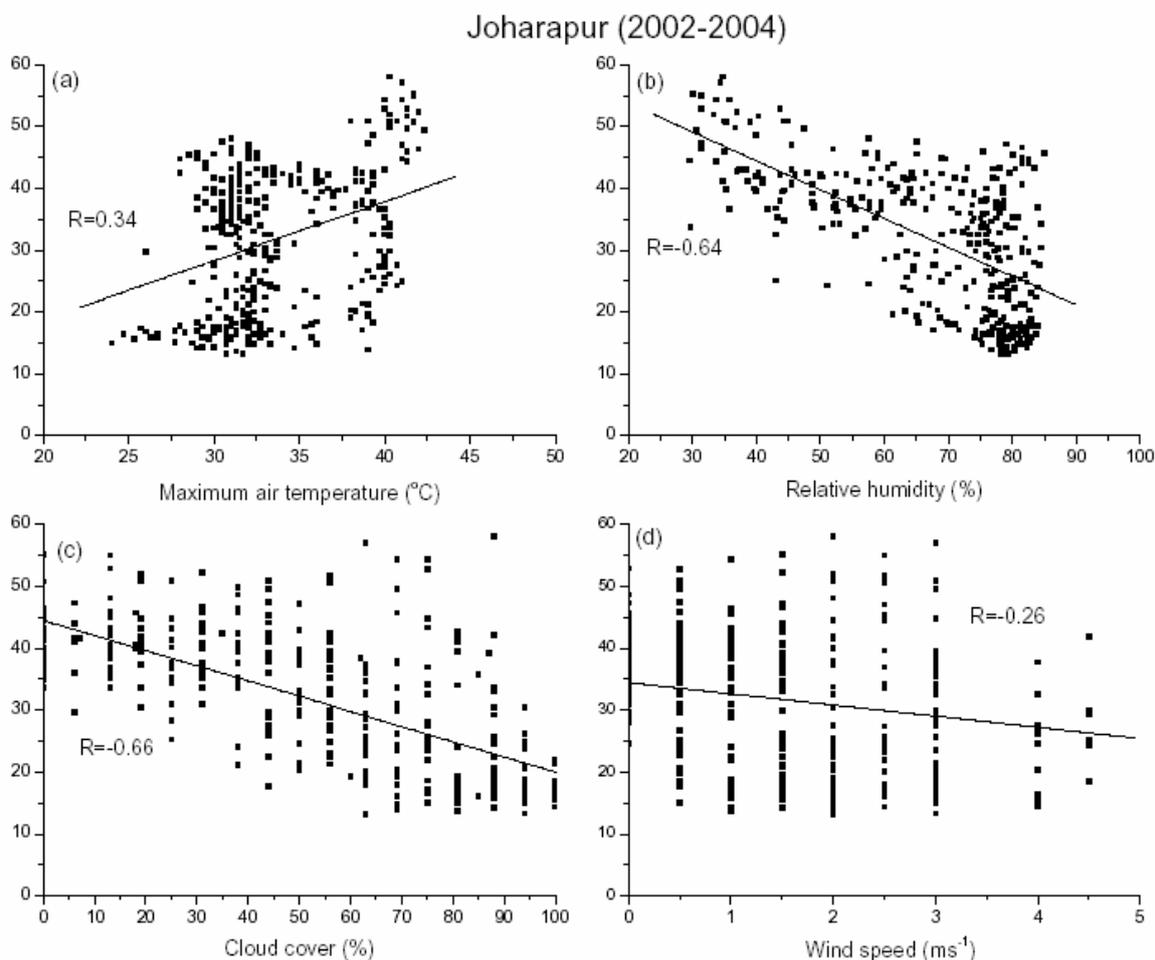
This indicates that O<sub>3</sub> decreases when cloud cover and RH increase, despite increased air temperature. Wind speed was about 4.5 m/s with a southwesterly direction during monsoon season and northeasterly of 1 m/s in winter and premonsoon seasons (Fig. 9f).



**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<sub>3</sub> 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<sub>3</sub>, 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<sub>3</sub> is 0.34, which is not as rich as expected; suggesting maximum O<sub>3</sub> 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<sub>3</sub>, which plays an important role in building up O<sub>3</sub>

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) ( $13.5^{\circ}N$ ,  $79.2^{\circ}E$ , 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 ( $28.6^{\circ}N$ ,  $77.2^{\circ}E$ , 216 m) and Ahmedabad ( $23^{\circ}N$ ,  $72.6^{\circ}E$ , 49 m) in India are higher to their respective rates during the morning hours (Table 5), which are attributed to the higher  $NO_x$

concentration from commuter vehicular emission, responsible for fast titration of O<sub>3</sub> in the evening (Naja and Lal, 2002). Thumba (8.6°N, 77°E, 2 m) a coastal site shows a morning rate of O<sub>3</sub> production higher, while evening rate is low compared to Joharapur.

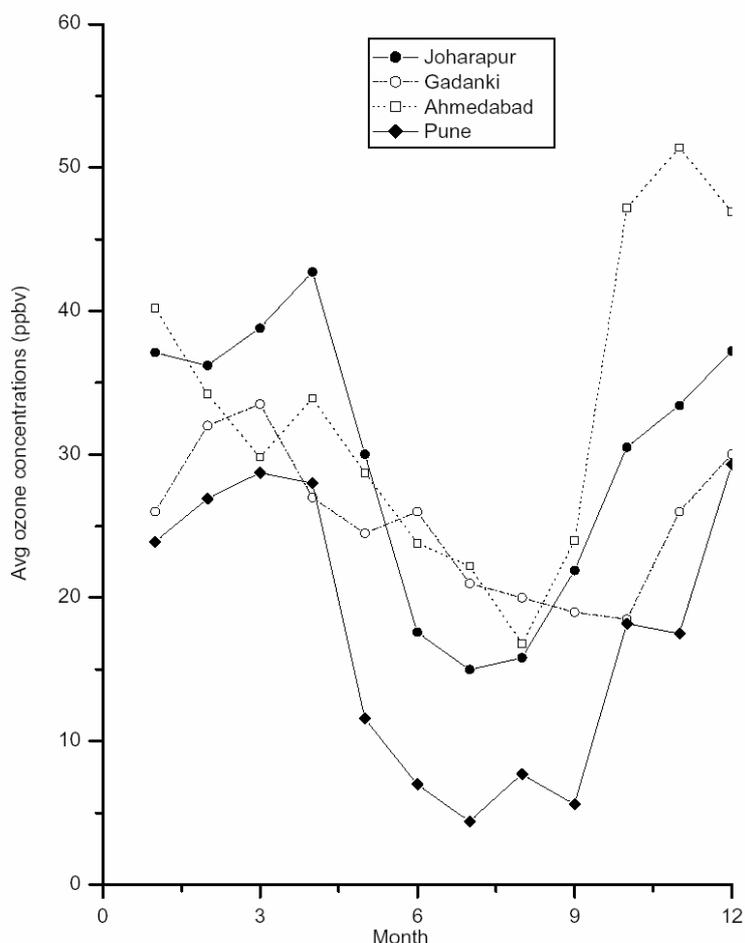
**Table 5.** Comparison of observed rate of change of O<sub>3</sub> concentrations at different sites in India.

Site	Rate of change at 0800 - 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<sub>3</sub> 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<sub>3</sub> at all sites; however, there are differences in O<sub>3</sub> concentration due to shifts in season from one site to another. The O<sub>3</sub> 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<sub>3</sub> during the southwest monsoon, while Gadanki extends into October due to northeast monsoon rain. The highest O<sub>3</sub> occurs in April at Joharapur due to intense solar radiation with a possible increase in precursors, which accelerate production of O<sub>3</sub> by photooxidation processes. The highest O<sub>3</sub> at Gadanki was observed in March. The low O<sub>3</sub> during monsoon at Joharapur is attributed to the low precursor concentrations and cloudy sky.

Average highest maximum O<sub>3</sub> in April at Joharapur is low (about 45 ppbv) compared to many global sites, such as the northern United States and China, where O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> measurements and meteorological parameters at Joharapur have shown that O<sub>3</sub> concentration varies with chemical parameters and meteorological conditions. The air temperature is positively, but poorly, related with O<sub>3</sub>, whereas cloud cover and relative humidity are negatively, but strongly, related. The wind speeds show poor negative relationship with O<sub>3</sub> concentration. The highest maximum O<sub>3</sub> 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<sub>3</sub> production involving complex and nonlinear photochemical chain reactions. There is a need for more extensive measurements of O<sub>3</sub> and precursor gases, especially NO<sub>x</sub> 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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