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Observational studies on the variations in surface ozone concentration at Anantapur in southern India

B. Suresh Kumar Reddy [a], K. Raghavendra Kumar [a], G. Balakrishnaiah [a], K. Rama Gopal [a], R.R. Reddy [a,*], Y. Nazeer Ahammed [b], K. Narasimhulu [c], L. Siva Sankara Reddy [a], Shyam Lal [d]

[a] Aerosol and Atmospheric Research Laboratory, Department of Physics, Sri Krishnadevaraya University, Anantapur-515 055, Andhra Pradesh, India
[b] Department of Physics, Yogi Vemana University, Kadapa-516 002, Andhra Pradesh, India
[c] Department of Physics, Govt First Grade College, Bellary, Karnataka, India
[d] Space and Atmospheric Sciences Division, Physical research Laboratory, Ahmedabad, 380 009, Gujarat, India

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ABSTRACT

Continuous measurements of surface ozone (O_3) at a semi-arid rural site (14.62°N, 77.65°E) in Anantapur, India during the period from December 2008 to July 2009 are presented. The diurnal variation in O_3 shows high concentrations (in the range of 25–77 ppbv) during daytime and low concentrations during late evening and early morning hours, due to slower titration of ozone by oxides of nitrogen (NO_x). The monthly average high (low) O_3 is 56.09 ± 10.1 ppbv (27.45 ± 2.3 ppbv) at noon in March (July), due to a possible increase in precursor gas concentration by anthropogenic activity and also due to the influence of local meteorological conditions. Furthermore, O_3 concentration has been observed as a function of season, which shows that the highest O_3 concentration is 52.05 ± 10.2 ppbv in the summer and the lowest 30.96 ± 5.7 ppbv in the monsoon season. The rate of the increase of surface ozone is high (2.11 ppbv/h) in March and low (0.32 ppbv/h) in July. Among the meteorological parameters, daily average ozone shows a significantly positive correlation with temperature ($R = 0.76$) and negative correlation with relative humidity ($R = -0.62$). Throughout the study period, high ozone concentrations were mainly associated with the winds from 150.5° to 260.1°. The weekend ozone effect indicates that higher O_3 concentration on weekend compared to weekday suggests that the photochemical production of O_3 is non-linear over this site. The results also show that high aerosol concentration has very strong impact on photochemical activities and ozone formation. The correlation between ozone and aerosol concentrations appears in a non-linear feature. Backward trajectory analysis shows that the increase of ozone concentration and the relatively constant high ozone concentrations during the summer might originate from the transport of ozone rich airmass above the boundary layer especially in Northern India and East Asian regions. On the other hand, the airmasses coming from the south over the Indian Ocean contributes low amount of ozone during the monsoon.

1. Introduction

Atmospheric ozone (O_3) plays an important role in the physico-chemical processes of the troposphere but it has also strong oxidant properties, which at certain ambient concentration levels, may cause damages to human beings, animals, and vegetation (Bates, 1994; Finlayson-Pitts and Pitts, 1997; Hogsett et al., 1997). The absorption of O_3 occurs in all regions of the respiratory system causing many health problems (Chang et al., 1991). The tropospheric O_3 is also important in determining the oxidizing capacity of the atmosphere, both through its direct role, and through its role as a precursor of the

* Corresponding author. Tel./fax: +91 8554 255710.
E-mail address: rajururreddy@gmail.com (R.R. Reddy).

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hydroxyl radical OH (Chand and Lal, 2004; Reddy et al., 2008b). The details of the chemistry of tropospheric ozone and its budget are described elsewhere (Kelly et al., 1984; Brasseur et al., 1999; Crutzen et al., 1999; Kley et al., 1999). The problem of tropospheric ozone changed dimensions about fifteen years ago, when it was realized that increased surface ozone was not only a local urban problem as an almost global increase of surface rural ozone concentrations, but also it was attributed primarily to photochemical production (Volz and Kley, 1998; Kalbokas and Repapis, 2004).

Surface ozone is produced through a complex set of photochemical reactions involving NO_x ($NO + NO_2$) and volatile organic compounds (VOCs) (Fishman and Crutzen, 1977, 1978). NO_x and VOCs are emitted from anthropogenic sources such as fossil fuel, power plants, industrial activities and transportation, as well as from natural sources such as lightning and soil (NO_x), and vegetation (biogenic VOCs such as isoprene). NO plays a critical role such that ozone production may occur even in a rural region, if the NO abundance is higher than that of a critical limit of about 10 pptv, a value that depends on ozone levels (Lin et al., 1988). Elevated concentrations of ozone are frequently observed over large rural areas in developed countries (Logan, 1989) due to anthropogenic activities and biogenic emissions (Kelly et al., 1984).

The existence of a back ground level of ozone in the atmosphere is well established. There is a considerable interest in quantifying surface background ozone concentrations and associated trends, as they serve to define a lower boundary with respect to the reduction of ozone by a control of anthropogenic precursors. Background ozone is generally defined as the fraction of ozone present in a given area that is not attributed to anthropogenic sources of local origin. As such, background ozone has several well documented sources, both natural and anthropogenic. These include: (1) downward transport of stratospheric ozone through the free troposphere to near ground level (2) in-situ ozone production from methane emitted from swamps and wetlands reacting with natural oxides of nitrogen (NO_x) (from soils, lightening strikes and downward transport of NO from stratosphere) (3) in-situ production of ozone from reactions of biogenic VOCs with natural NO_x and (4) long range transport of ozone from distant pollutant sources (Varotsos and Caratlis, 1991; EPA, 1993; Vingarzan and Thompson, 2004; Reddy et al., 2008b).

Two mechanisms have been proposed to account for the high rural ozone (Subbaraya and Lal, 1998; Naja and Lal, 2002). One is the transport of O_3 from urban areas, and the other is the transport of its precursors, NO_x (nitric oxide, NO, and nitrogen dioxide, NO_2), and non-methane hydrocarbons (NMHC) (Trainer et al., 1987), followed by in-situ or in-transit photochemical ozone production. The latter depends critically on the concentration of NO (Glavas, 1999). The resulting ozone concentrations depend sensitively upon the meteorological parameters such as temperature, cloudiness, sunlight, wind speeds and the mixed layer depth. Therefore, changes in these meteorological parameters due to climate change will necessarily affect surface ozone concentrations. However, the direction of change itself is often unclear because of multiple competing effects (Racherla and Adams, 2007).

In order to understand ozone chemistry and transport at a semi-arid rural site in India, a program was initiated at Sri Krishnadevaraya University (SKU), India (14.62°N, 77.65°E, 331 masl) (Fig. 1) situated at the southern edge of Anantapur, for the measurements of ozone under the Indian Space Research Organization (ISRO), Department of Space, Bangalore. The present paper records on the measurements of diurnal variations of surface O_3 in different months that have been studied in the light of changes in meteorological parameters.

2. Measurement site and general meteorology

The measurement site SKU, a semi-arid rural station in Anantapur is surrounded by a number of cement plants, lime kilns, slab polishing and brick making units (see Fig. 1). Beside these industries, the national highways (NH 7 and NH 205) and the town area etc., that are situated in the north to southwest sides of the sampling site, release large quantities of particulate matter every day into the atmosphere (Ahammed et al., 2006; Kumar et al., 2009a). The Anantapur site is about 200 km and 350 km from the two nearby major cities, Bangalore (12.5°N, 77.4°E) to the southwest and Hyderabad (17.4°N, 78.4°E) to the northeast, respectively. Both contribute to the enhancement of O_3 precursor gases in these areas.

Anantapur represents a very dry continental region of Andhra Pradesh, India. It is geographically situated on the boundary of a semi-arid and rain shadow region. The climate here is hot and dry in the summer (March to May), hot and humid during the monsoon (June to November) and dry in the winter season (December to February). The most prominent meteorological feature here is the monsoon rainfall activity (June–September) amounting to 80% of the total normal annual rainfall, which is mostly related to diurnal and seasonal variations of O_3. This region receives very little rainfall, and the average annual rainfall is of 450 mm during the whole year (about 300 mm during the southwest monsoon period and 150 mm in the northeast monsoon period) (Kumar et al., 2009b). Southwest winds bring the monsoon, which sets in by the first week of June and lasts until September (Asnani, 1993). The weather during the post-monsoon season (October–November) is calm with scattered clouds and partial rainfall occurs sometimes. Fair weather conditions prevail during the winter season (December–February) with calm wind speeds on the order of 1–2 m/s in a northeasterly direction and with clear sky and moderate relative humidity (RH) of 20–70%. The summer season (March–May) experiences hot weather due to intense solar radiation. The surface air maximum temperature is about 42 °C at noon and minimum 20 °C in the morning.

3. Experimental technique

Surface ozone is measured using an analyzer (O_3 41 M; Environnement s.a., France) based on absorption of ultraviolet (UV) radiation at 253.7 nm by ozone molecules. Contribution by other species in the absorption and scattering of the radiation in the cell is eliminated by comparing the measurement with ozone free air in reference mode. Systematic and regular measurements of surface ozone have been made at Anantapur with the ozone analyzer. The instrument is kept at a height of ~12 m from the ground level and a five-meter long

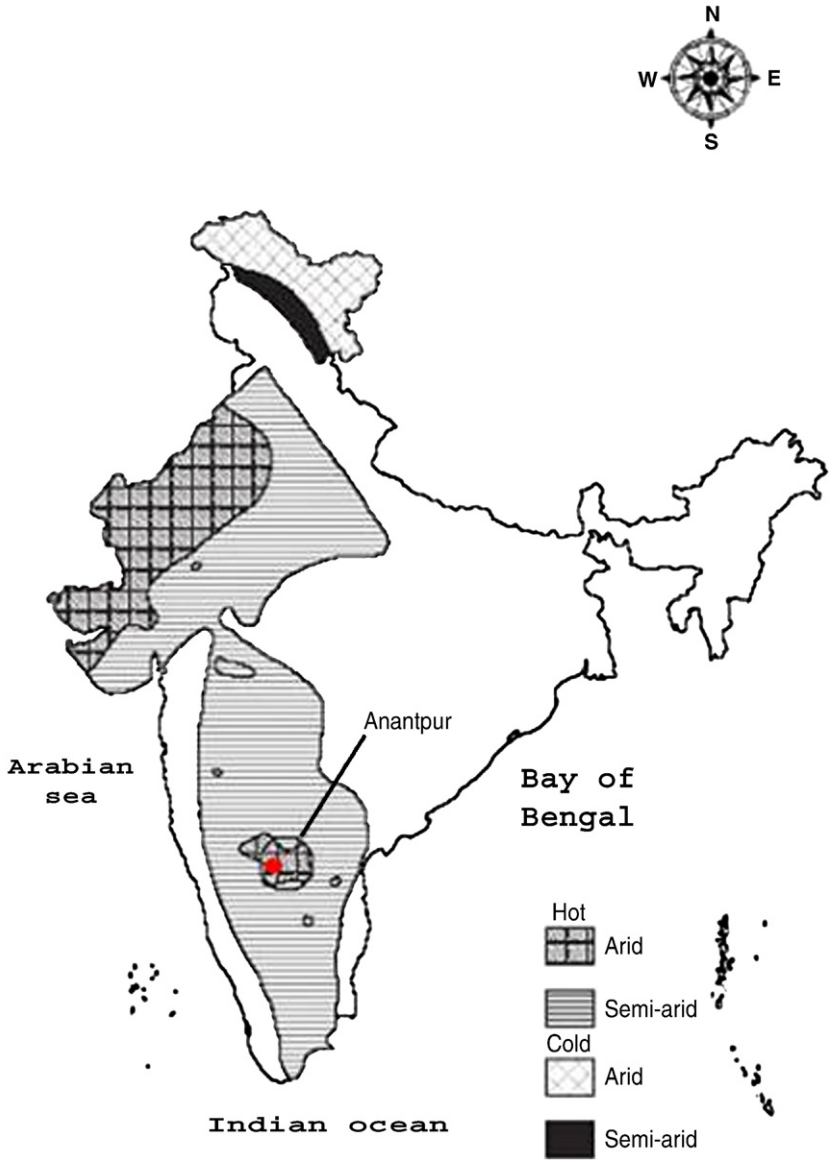


Fig. 1. Geographical map of Indian subcontinent showing the location of Anantapur, a hot semi-arid site. The solid dot (red color) points the sampling site SKU (14.62°N, 77.65°E).

teflon tube is arranged as the intake tube for taking the outside air sample, with a particulate filter to prevent particles from entering the instrument. An inverted teflon funnel is fitted at the entrance of the tube to avoid the dust and rainwater from entering the tube and the systems. A mercury lamp is the source of this radiation that is absorbed by the ozone molecules present in the ambient air filled in the absorption cell of length of about 60 cm. The absorbed signal as well as the reference signal is measured by a detector. Ozone concentration is estimated using the Beer–Lambert law. This is kept at constant temperature and, based on the lamp intensity (by changing the current to the UV lamp), the concentration of O_3 varies. A built-in ozone generator is employed in this instrument. The calibration is carried out until the preset values of reading in the analyzer match the current applied to the UV lamp.

The O_3 determination is based on a commercial instrument using UV mercury absorption of 253.7 nm radiation. The O_3 analyzer is so designed that it absorbs ozone at 253.7 nm, and the UV mercury lamp fixed in the instrument also emits light of the same wavelength. The calibration factor is not required in this process. The detector is employed before and after the absorption takes place in the fixed length flow path, so the variations in the intensity of the light are balanced. In order to check the zero reading of the analyzer, zero air has to be admitted which is free of ozone. If the analyzer reads higher value for zero air, then the ozone scrubber in the analyzer will be changed. Also the analyzer scrubber continually checks the zero every 10 s and goes to the sample line. These are reformed for 15 min each on a daily basis for an initial period of 1 year and then once in every 3–4 weeks afterwards. The minimum detection limit of the analyzer is about 1 ppbv and its response

is about 10 s (Reddy et al., 2008b). Lal et al. (1998, 2000) and Nair et al. (2002) have also employed the same O_3 analyzer described above in their study. The absolute accuracy of these types of system is reported to be 5% (Kleinman et al., 1994).

4. Results and discussions

4.1. Diurnal variations in surface ozone

The monthly average diurnal variations of surface ozone observed at Anantapur during the study period are shown in Fig. 2. The vertical bars in the figure denote the $\pm 1\sigma$ standard deviation. The diurnal variations of O_3 at this sampling site are characterized by high concentration (25–77 ppbv) during the daytime and low concentration (5–27 ppbv) during the late evening and early morning hours. The minimum O_3 concentration of about 23.52 ± 3.5 ppbv is noticed during the early morning around (05:00–07:00 h) in the month of July. From then on, the O_3 concentration starts increasing gradually just after sunrise coinciding with the solar radiation increasing, and it reaches the maximum value of 77.35 ± 10.2 ppbv at around (15:00–16:00 h) in the month of March. It decreases rapidly after peak until evening, and then keeps decreasing gradually, maintaining low values over night hours due to lack of solar radiation. The similar diurnal variation pattern of O_3 was observed at the Joharapur site in western India (Debaje and Kakade, 2006) and in another rural site Gadanki in southern India (Naja and Lal, 2002) and in numerous urban areas around the world (Lal et al., 2000; Mazzeo et al., 2005; Tu et al., 2007). The contour plot of long-term variations in surface ozone diurnal cycles has also been shown in Fig. 3.

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 the daily changing major precursor concentrations from various natural and anthropogenic sources and through the variable influence of meteorological parameters. The low O_3 concentrations observed at night are due to the absence of photolysis of NO_2 and the continuous loss of O_3 by NO_x titration. Further, the continuous loss of O_3 by dry and wet depositions results in the minimum O_3 at sunrise.

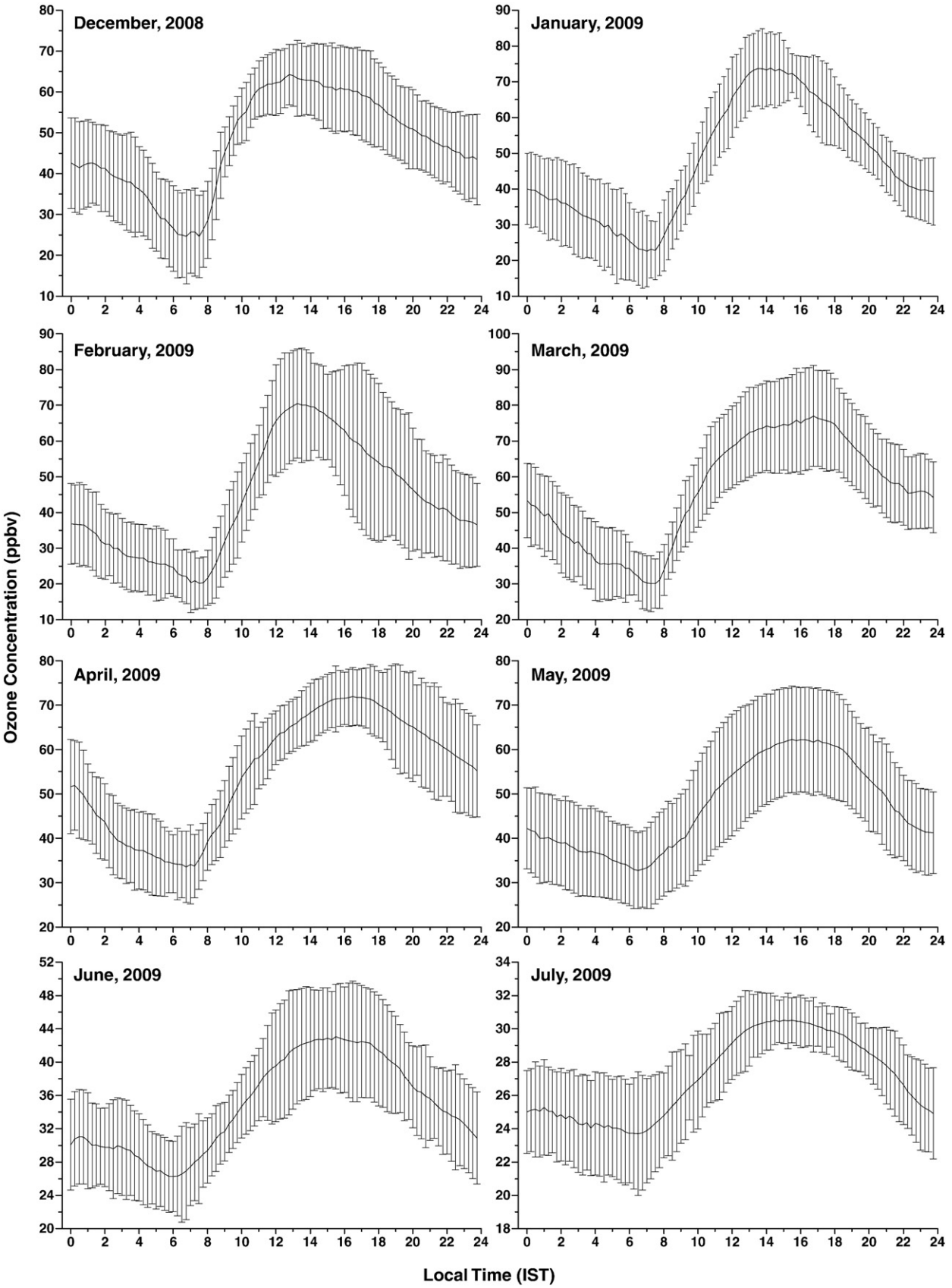
Daytime maximum ozone mixing ratios exhibit changes in pattern at different times of the year because of the variations of photoxidation of precursor gases (Fishman and Crutzen, 1978; Lin et al., 1988; Naja and Lal, 2002). Besides the photochemical reactions affected by solar radiation and variation in anthropogenic emissions, boundary layer process and meteorological parameters also play an important role in the variabilities of ozone. During nighttime, the boundary layer descends and remains low until early morning and more stable atmospheric conditions exist, the air in the surface layer resists to mixing with that in the upper layer. It is very hard for ambient air pollutants to disperse; so they are trapped in the shallow surface layer and thus show high concentration which leads to low concentration of ozone during late night and early morning hours. After sunrise, boundary layer height gradually increases from about 200–300 m to about 1500–2000 m during noon hours and get maximum value due to convective heating, and the layer becomes less stratified. During this time, the ambient air becomes unstable and rises due to heating of the earth surface by solar radiation. Thus the dispersion of air pollutants accelerates and the mixing of low ozone amount air in the surface layer with high ozone amount air in the upper layer also gets faster (Lal et al., 2000; Shan et al., 2008). Therefore, average ozone mixing ratios during 12:00–14:00 h could be representative of the upper boundary layer and the free lower tropospheric ozone levels. The photochemical production of ozone is directly connected to the temperature and the solar flux, its concentration increases with respect to both parameters. For instance, transported Peroxy Acetyl Nitrate (PAN), anthropogenic carbon monoxide, methane and less reactive hydrocarbons can be considered as responsible for the observed ozone maximum/minimum in the background troposphere and at remote sites away from man-made polluted sources.

4.1.1. Comparison of surface ozone with other sites in India

Fig. 4 shows a comparison of monthly mean variations of ozone concentrations observed at a rural site, Anantapur along with seven different rural and urban stations such as Gadanki (rural; 13.5°N, 79.2°E, 375 masl; Naja and Lal, 2002), Mt. Abu (high altitude; 24.6°N, 72.7°E, 1680 masl; Naja et al., 2003), Ahmedabad (urban; 23°N, 72.6°E, 49 masl; Lal et al., 2000), Pune (urban; 18.32°N, 73.51°E, 559 masl; Shende et al., 1992), Delhi (urban; 28.7°N, 77.2°E, 220 masl; Shende et al., 1992), Thumba (coastal; 8.6°N, 77.1°E, 2 masl; Nair et al., 2002), Tranquebar (11°N, 79.9°E, 9 masl; Debaje et al., 2003) and Joharapur (rural; 19.22°N, 75°E, 581 masl; Debaje and Kakade, 2006). The diurnal variations in the ozone observed at the rural site show an asymmetric diurnal cycle. However, measurements made at urban sites exhibit symmetric diurnal variations in ozone. Differences in O_3 at different sites in India are due to the differences in the concentrations of precursor gases, chemical processes, anthropogenic activities prevailing in the concerned areas and meteorological parameters.

The comparison of seasonal variations in ozone observed at both urban and rural sites in general, shows a similar pattern of monthly variation in O_3 in all sites. However, there are differences in O_3 concentration due to shifts in season from one site to another. All seven sites along with the rural site in Anantapur, exhibit low ozone mixing ratios during the monsoon season. After the monsoon, ozone concentrations increase sharply at Anantapur, Mt. Abu, Gadanki and Ahmedabad. The highest O_3 occurs in March and April at Anantapur (about 50–56 ppbv) compared to all other stations. It is due to the availability of intense solar radiation with a possible increase in precursors, which accelerate the production of O_3 by photoxidation processes. Interestingly, measurements made at Delhi show maximum ozone mixing ratios during May (Shende et al., 1992). A high annual average ozone

Fig. 2. Diurnal variations of average ozone mixing ratios in different months for the period December 2008–July 2009 measured at Anantapur. Vertical bars are $\pm 1\sigma$ standard deviation in monthly averages.


December, 2008
January, 2009
February, 2009
March, 2009
April, 2009
May, 2009
June, 2009
July, 2009
Ozone Concentration (ppbv)
Local Time (IST)

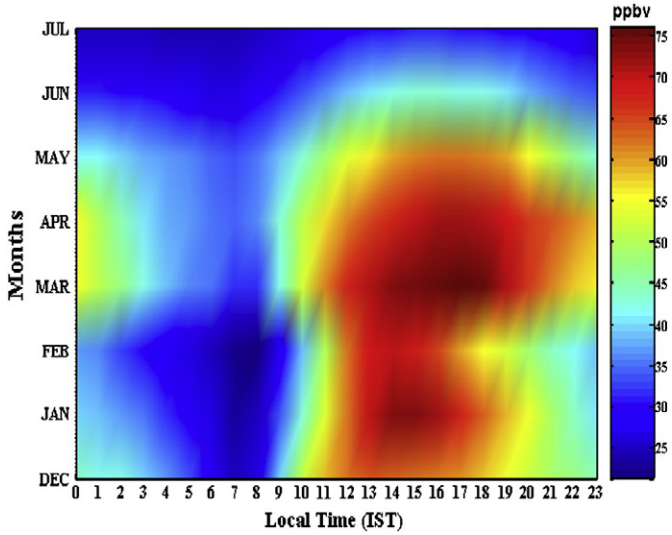


Fig. 3. Temporal variations of ozone concentrations at Anantapur for the study period.

mixing ratio is observed both at Anantapur and Mt. Abu in comparison to Gadanki, Ahmedabad, Pune, Joharapur and Delhi. These differences are related to the availability of solar radiation and high concentrations of precursor gases, which are caused by local emissions or transport from the regional sources, and the Stratosphere–Troposphere Exchange (STE) (Reddy et al., 2008a).

4.2. Rate of change of ozone

Table 1 shows monthly mean O_3 concentrations and rate of change of ozone [$d(O_3)/dt$] in the morning hours (08:00–11:00 h) and evening hours (17:00–19:00 h) at Anantapur for the study period. The high O_3 concentrations (56.09 ± 8.2 ppbv) were observed in March, while low concentrations (27.46 ± 1.8 ppbv) occurred in July, attributable to variations in precursor gases and thus indicate the influence of changing meteorological parameters. The morning average O_3 rate of change is 4.68 ppbv/h which may be considered as higher and is due to fast production of O_3 by freshly emitted precursors; whereas it is low (-2.50 ppbv/h) in the evening because of the low production of NO_x at this site (as compared to the urban site). This is a unique characteristic feature of the rural environment (Ahammed et al., 2006).

4.2.1. Comparison of the rate of change of ozone

Table 2 shows a comparison of the rate of change of O_3 at Anantapur and these observations made at different sites in India. The average rates of change of ozone during the evening hours (17:00–19:00 h) at Anantapur are estimated to be -2.5 ppbv/h, which are similar to those of the rural site Gadanki (-2.6 ppbv/h), thereby indicating that Anantapur is more polluted than Gadanki (see Table 2). It is clearly evident from the brick making units, stone crushing machines and the cement

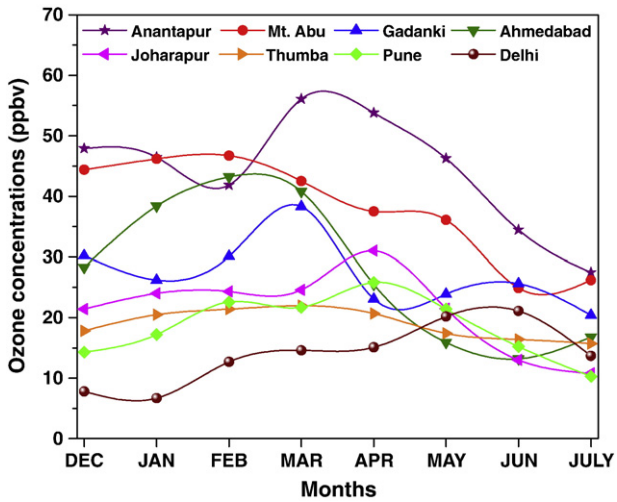


Fig. 4. Comparison of monthly variations in ozone concentrations observed at different stations in India.

Table 1
Monthly average ozone concentrations with ±1σ standard deviation and rate of change of ozone during morning and evening hours for the study period at Anantapur.

Month	Ozone concentration (ppbv)	Rate of change at (08:00–11:00 h) ppbv/h	Rate of change at (17:00–19:00 h) ppbv/h
December — 08	47.91 ± 5.63	5.65	−2.73
January — 09	49.45 ± 7.32	8.51	−4.39
February — 09	51.71 ± 9.53	7.23	−3.81
March — 09	56.09 ± 8.21	6.19	−2.83
April — 09	53.81 ± 5.72	4.52	−2.42
May — 09	46.25 ± 8.91	2.57	−1.83
June — 09	34.46 ± 3.96	1.98	−1.29
July — 09	27.46 ± 1.84	0.81	−0.62
Average	45.93 ± 4.12	4.68	−2.50

Table 2
Observed rate of change of O_3 concentration (ppbv/h) at Anantapur with different sites in India.

Site	Rate of change of O_3 at 08:00–11:00 h (ppbv/h)	Rate of change of O_3 at 17:00–19:00 h (ppbv/h)	Reference
Anantapur	4.6	−2.5	Present study
Ahmedabad	5.9	−6.4	Lal et al. (2000)
Thumba	5.5	−1.4	Nair et al. (2002)
Pune	4.8	−2.6	Shende et al. (1992)
Gadanki	4.6	−2.6	Naja and Lal (2002)
Delhi	4.5	−5.3	Ahammed et al. (2006)
Joharapur	4.5	−3.3	Debaje and Kakade (2006)
Tranquebar	3.1	−2.8	Debaje et al. (2003)

industries established and the National highways around the site. The average rate of change of O_3 during the hours 17:00–19:00 h at Anantapur, Gadanki, Pune and Thumba is estimated to be −2.5 ppbv/h, −2.6 ppbv/h, −2.6 ppbv/h and −1.4 ppbv/h, respectively. Which are lower in magnitude (35–45%) than their respective production rates during the hours 08:00–11:00 h (see Table 4). The rates of change of O_3 during the hours of 17:00–19:00 h at urban sites, Ahmedabad (−6.4 ppbv/h) and Delhi (−5.3 ppbv/h) are higher and are almost similar (8–18% in magnitude) to their respective rates during the hours of 08:00–11:00 h (Table 2). These are attributed to the higher NO_x concentration from vehicular emission, and also due to the fast titration of O_3 in the evening (Naja and Lal, 2002). This feature of ozone variations distinguishes the urban and rural sites. NO_x levels are about 10 times higher at Ahmedabad than those at Anantapur (Ahammed et al., 2006). Thumba, a coastal site, shows a morning rate of change of O_3 production higher, while the evening rate is low compared to Anantapur (Table 2). This indicates that Anantapur is more polluted as compared to Thumba, and it is less polluted as compared to Ahmedabad and Delhi.

4.3. Seasonal variations in surface ozone

Fig. 5 shows diurnal variations of mean ozone during the three different seasons, namely winter (December–February), summer (March–May) and monsoon (June–September). In all the seasons there is a similar pattern, which becomes more distinct in winter and summer; however, the amplitudes of the variations are different. The amplitude, which is the difference in O_3 concentration between daytime and nighttime, is the highest in summer and the lowest in monsoon. Daytime ozone mixing ratios are observed to be maximum (about 70 ppbv) during the summer and minimum (about 27 ppbv) in the monsoon period. The concentration of ozone during the winter period increased from a minimum value of 25 ppbv at around 08:00 h, to a value of 60 ppbv at noon time. However, during the summer season the minimum ozone value was 35 ppbv, which rose to a maximum value of 70 ppbv. The highest ozone concentrations were observed both in the winter and summer seasons but not in the monsoon months. This indicates that the ozone variation is not only controlled by solar radiation, but also by dynamics. Favorable conditions for photochemical O_3 production are high temperature, high intensity of solar radiation, and sufficiently high concentrations of NO/NO_x (Naja and Lal,

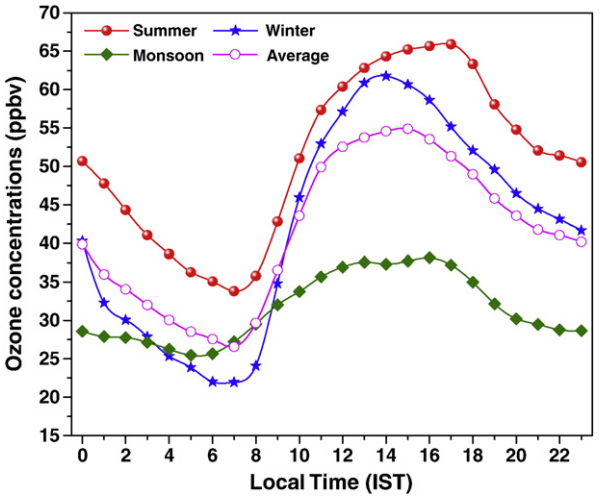


Fig. 5. Season-wise diurnal variations of average ozone concentrations at Anantapur.

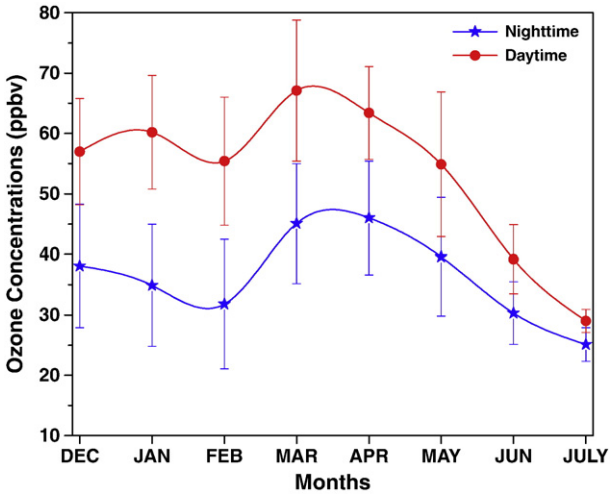


Fig. 6. Average mixing ratios of ozone during nighttime and daytime in different months.

2002). All these conditions are satisfied at our site during the summer season, resulting in the observed broad ozone maximum. There is also the possibility of enhanced transport from the stratosphere during this season.

A relatively lower amount of surface ozone was observed during the monsoon months than the winter/summer months. It is worth mentioning that low O_3 levels are noticed in all seasons during morning hours because the lower boundary layer height largely reduces the mixing processes between the ozone-poor surface layer and the ozone rich upper layer. The increase of ozone in the troposphere is the result of increase in human-produced ozone precursor emissions. Ozone concentrations are found to be increasing in the free troposphere as well as near the surface in many parts of the northern hemisphere (Lal et al., 2000; Varotsos et al., 2001; Nair et al., 2002; Naja and Lal, 2002; Debaje and Kakade, 2006).

4.4. Changes of surface ozone during daytime/nighttime

The monthly average ozone mixing ratios of surface ozone during daytime/nighttime for the period December 2008–July 2009 at Anantapur was shown in Fig. 6. Out of 24 h we have separated (08:00–20:00 h) as daytime and (20:00–08:00 h) as nighttime changes of O_3 for the period of study. The monthly average O_3 concentrations show a daytime maximum (67.13 ± 11.7 ppbv) in March and minimum (29.16 ± 1.9 ppbv) in July, and corresponding nighttime maximum (46.18 ± 9.9 ppbv) and minimum (25.15 ± 2.8 ppbv) with $\pm 1\sigma$ standard deviation. The daytime increase in ozone mixing ratio is basically due to photoxidation of precursor gases, like CO, CH_4, and other hydrocarbons in the presence of a sufficient amount of NO/NO_x (Debaje et al., 2003). The increase rate of average O_3 concentration in the daytime (08:00–20:00 h) and nighttime (20:00–08:00 h) at Anantapur for the study period was shown in Table 3. The average high O_3 concentrations (56.09 ± 8.2 ppbv) were noticed in March while low concentrations (27.46 ± 1.84 ppbv) occurred in July. It is due to the variations in precursor gases and influence of changing meteorological parameters. The rate of increase of O_3 is high (2.11 ppbv/h) in March and low (0.32 ppbv/h) in July. The average rate of increase of O_3 from midnight to midday is 1–1.5 ppbv/h (Reddy et al., 2008b).

Table 3
Monthly average O_3 concentrations with $\pm 1\sigma$ standard deviation observed at Anantapur during nighttime (20:00–08:00 h) and daytime (08:00–20:00 h) and its increase rate for the study period.

Month	Average O_3 during nighttime (ppbv)	Average O_3 during daytime (ppbv)	Increase O_3 rate (ppbv/h)
December — 08	38.13 ± 10.23	57.02 ± 8.85	1.57
January — 09	34.91 ± 10.17	60.21 ± 9.47	1.83
February — 09	31.84 ± 10.72	55.46 ± 10.68	1.97
March — 09	46.18 ± 9.96	67.13 ± 11.72	2.11
April — 09	45.04 ± 9.42	63.48 ± 7.73	1.45
May — 09	39.65 ± 9.82	54.91 ± 12.03	1.27
June — 09	30.38 ± 5.28	39.28 ± 5.76	0.74
July — 09	25.15 ± 2.83	29.16 ± 1.93	0.32

4.5. Weekday–weekend effect

The diurnal hourly average for the study period was computed from hourly averages of O_3 concentration for Monday through Friday as weekday O_3, and for Saturday through Sunday as weekend O_3. The hourly average maximum ozone concentration at noon was also computed for monthly weekend and weekday. From monthly, the seasonal mean of weekend and weekday O_3 was computed for different seasons during the study period. Fig. 7 shows hourly average of the seasonal diurnal variation of weekend and weekday O_3 concentrations during the three seasons of winter, summer and monsoon as stated in Section 4.3, at the rural site. Seasonal averages are computed for the weeks in which weekend ozone was higher than that of the weekday ozone. Fig. 7 shows that the highest maximum O_3 concentrations observed were about 70 ppbv on weekend and 65 ppbv on weekday at around 16:00 h in the summer. The corresponding next highest O_3 concentration of 62 ppbv and 56 ppbv was observed at around 14:00 h in the winter. The diurnal variation of O_3 was 34 and 41 ppbv respectively in the monsoon season on weekday and

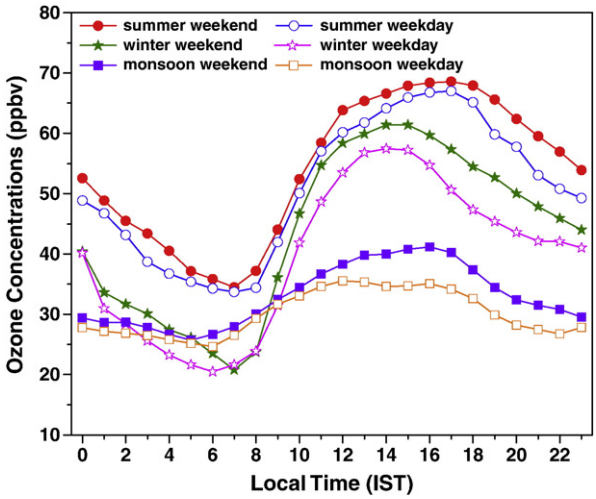


Fig. 7. Seasonal and diurnal variations of ozone concentrations on weekend and weekday at the rural measurement site, indicating that ozone is higher on weekend.

weekend at around 16:00 h and it is due to cloudy and rainy weather. However, O_3 concentration was higher on weekend than weekday by about 5–7 ppbv, due to less NO_x titration at the rural site (Fig. 7).

During the winter season, the average O_3 concentrations on weekday and weekend started to increase after the monsoon season because of less cloud cover and favorable meteorological conditions for photochemical production of O_3. The difference between weekday and weekend ozones was observed to be less; however, weekend ozone concentration was still higher than weekday. The higher O_3 concentration on weekend was maintained from morning throughout day and nighttime in all seasons. The higher O_3 on weekend is due to decreased NO_x emission that resulted in less NO_x titration of O_3. Qin et al. (2004) reported that VOCs sensitivity combined with a decrease in weekend NO_x emissions, caused the weekend O_3 effect. Decreased anthropogenic VOC emission appears to increase isoprene reactivity, which possesses high MIR (Carter, 1994). The photochemical production of O_3 depends on its precursor gas concentration mainly on NO_x and VOC sensitivity. The emission of isoprene from trees at the rural site was related to the ambient temperature (Benjamin et al., 1997), which was the highest in the afternoon. Emission of NO_x depends on anthropogenic activity mainly during daytime. Therefore, the O_3 peak appeared mostly in the afternoon at the rural site probably because of the availability of precursor gases (isoprene) for photochemical production of O_3 in the afternoon (Debaje and Kakade, 2006). Multi-day timescale required for chemical processing and transport lead to elevated ozone levels under photochemical episode conditions, and carryover of ozone and its precursors on Friday and Saturday nights (Qin et al., 2004). However, the mechanisms for the weekend effect on ozone formation are still not well understood.

Fig. 8 shows the frequency distribution of O_3 concentrations (ppbv) in different ranges for the study period (December 2008–July 2009) at Anantapur. There are a total

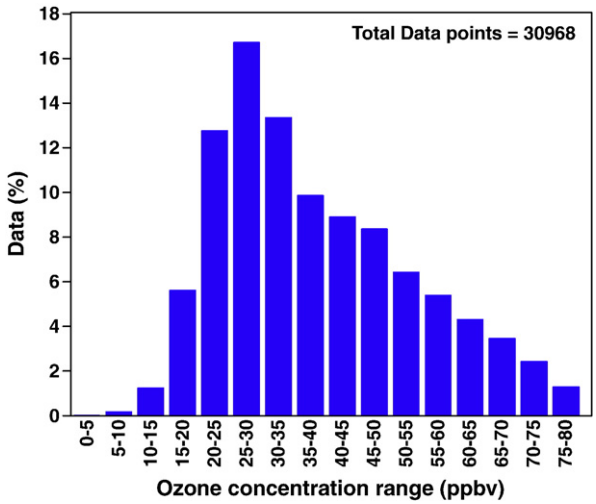


Fig. 8. Frequency distribution of O_3 concentrations (ppbv) for the measurement period December 2008–July 2009 observed at Anantapur.

Table 4
Monthly average O_3 concentrations, air temperature, relative humidity, wind speed, direction and total rainfall with $\pm 1\sigma$ standard deviation observed for the study period December 2008–July 2009 at Anantapur.

Month	Ozone concentration (ppbv)	Air temperature (°C)	Relative humidity (%)	Wind speed (m/s)	Wind direction (deg)	Rainfall (mm)
December — 08	47.91 ± 5.63	23.53 ± 0.65	50.27 ± 2.57	1.79 ± 0.26	212.03 ± 22.21	0
January — 09	49.45 ± 7.32	25.32 ± 1.05	43.98 ± 3.89	1.44 ± 0.25	153.37 ± 21.36	0
February — 09	51.71 ± 9.53	27.23 ± 0.98	38.98 ± 3.16	1.58 ± 0.24	157.81 ± 19.29	0
March — 09	56.09 ± 8.21	29.76 ± 0.94	34.56 ± 2.88	1.54 ± 0.24	166.79 ± 19.42	0
April — 09	53.81 ± 5.72	32.22 ± 0.87	35.55 ± 2.92	1.82 ± 0.25	193.55 ± 17.19	0
May — 09	46.25 ± 8.91	31.34 ± 0.85	48.03 ± 3.22	2.07 ± 0.24	243.59 ± 11.61	118.0
June — 09	34.46 ± 3.96	28.81 ± 0.68	59.26 ± 2.75	1.63 ± 0.28	290.91 ± 9.21	18.0
July — 09	27.46 ± 1.84	27.83 ± 0.59	60.86 ± 2.47	2.61 ± 0.25	310.12 ± 9.16	10.0

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

of 5156 recorded data points during the observation period. It shows that 60% of all O_3 concentrations lie in the range of 20–50 ppbv and 35% lie in the range of 50–80 ppbv. The remaining 5% of ozone concentration lie in the 10–20 ppbv range. It also shows that the highest 22% of all O_3 measurements lie in the 30–40 ppbv range, and the lowest 5% measurements lie in the 10–20 ppbv range.

4.6. Influence of meteorological parameters on ozone concentration

Meteorological conditions play an important role in ozone formation, transfer and dispersion. Variations of local meteorological conditions, such as solar radiation, air temperature, wind speed, direction, rainfall and relative humidity (RH), can greatly affect the temporal variations of ozone. Table 4 summarizes average monthly variations of O_3 with air temperature, relative humidity, wind speed, direction and rainfall for the study period. The highest O_3 of about 56.09 ± 10.4 ppbv in March was due to high air temperature (40 °C) whereas; the lowest of 27.45 ± 2.3 ppbv in July was due to low ambient air temperature (27 °C) and less precursor concentration. However, the highest average maximum air temperature that was observed in April is 32 °C for which the corresponding O_3 observed is 53.81 ± 5.7 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 and high NO_x production play a predominant role in reduced O_3 production in the months of April and May. The concentrations of O_3 observed in the months of July (27 °C) and January (26 °C) are 27.46 ± 1.8 and 49.45 ± 7.3 ppbv, respectively. High concentrations of O_3 in January are not due to high sunshine but also by dynamics. In April, the rate of natural hydrocarbon (isoprene) emissions from plants as a function of ambient air temperature and solar radiation (Poisson et al., 2000; Petron et al., 2001), which is highly reactive, possibly accelerates O_3 production. Sillman and Samson (1995) noticed that O_3 concentration increases with air temperature in both urban and rural environments.

The increase in RH observed from March to July was from 35 to 60%, and corresponding decrease in O_3 was from 56.09 ± 8.21 down to 27.46 ± 1.84 ppbv. Similarly, the decrease in RH from 50 to 34% was observed from December to April, and related O_3 concentration increased from 47.91 ± 5.63 to 53.81 ± 5.72 ppbv (Table 4). Keen observation of the results reveals that the highest O_3 concentration of 56.09 ± 8.21 ppbv obtained in March at the time of the lowest RH is 34%. This indicates a negative impact of RH on photochemical production of O_3 in this environment. On the other hand, RH is higher during the rainy season which

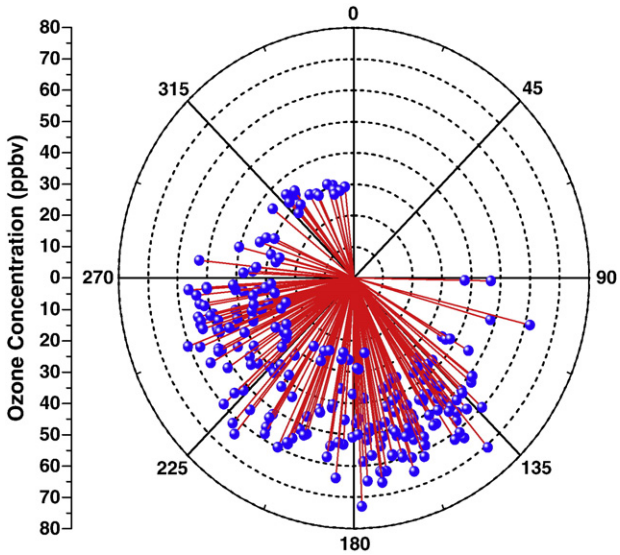


Fig. 9. Daily ozone concentrations according to wind directions for the observation period (December 2008–July 2009).

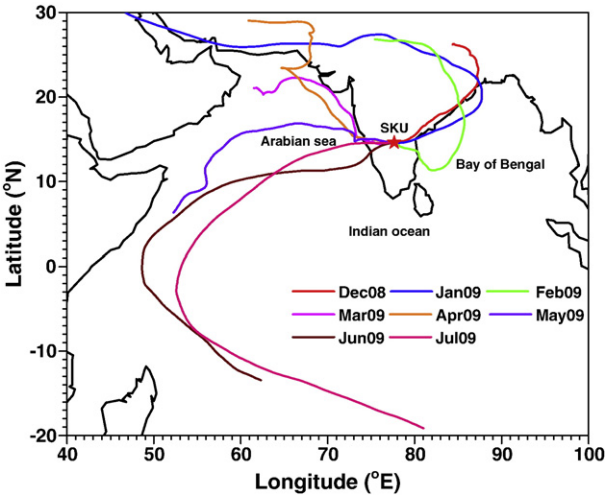


Fig. 10. Seven-days backward trajectories of airmasses for a typical day in different months at 500 m altitude during the study period.

shows a negative correlation with temperature and ozone mixing ratio. The southwest monsoon, which starts by the end of May, is quite active during June, July and August and becomes weak by September. During October and November, northeast monsoon prevails. During the monsoon period, the sky is generally overcast, decreasing the solar insulation thereby reducing the photochemical processes. Also during the rainy season some of the pollutants are washed out. These two factors could cause low levels of ozone during monsoon period. The low ozone levels in July may be due to the short sunshine duration and more rainfall during this period (Shan et al., 2008). More than half of the days during July and August showers will continue and even less was observed during the other months of the year. The highest rainfall (118 mm) is recorded in May and no rainfall is expected from December to April. High RH during July was associated with the numerous rainy days.

Wind speed was about 5–6 m/s with a southwesterly direction during the monsoon season and northeasterly of 2 m/s an average in winter and summer seasons. The variation of monthly wind speed shows high values from April to June, and then a sharp decrease to the minimum level in July. It is pertinent to mention that high ozone concentrations during the study period are associated with the winds from 150.5° to 260.1° (see Fig. 9), which may be explained by the geographical location of the site (Fig. 1). The average concentration of O_3 increases steadily with the wind speed increasing from $\leq$1 to 2–4 m/s, while it drops a little when the wind speed is higher than 4 m/s. Higher wind speeds reduce the stability of the boundary layer; and thus the intrusion of O_3 in the upper layer to the surface layer gets faster and increases the concentration of surface O_3. However, when the wind speed is too high, the high dispersion of O_3 could offset the contributions from the upper layer (Tu et al., 2007). Generally speaking, the levels of industrialization and urbanization are distinctly higher in the northern region than those in the southern region. So the airmasses coming from north/northwesterly associated directions might bring more pollutants to the observation site in the summer. On the other hand, the airmasses coming from the south/southwesterly directions during the monsoon season might originate from the Indian Ocean. They pass over the Arabian Sea and bring relatively clean air. Therefore, winds from the north/northwesterly directions are associated with highest averaged ozone concentrations. In addition, high ozone concentrations associated with the northern wind may be due to the transport of pollutants from East Asian region. However, high ozone concentrations seem to have no obvious correlation with a given wind direction in the summer (transition period for winds). This may be due to the changing synoptic condition and complicated meteorological effects on ozone production, especially with the influence of rainfall. Numerous rainy days during the summer have weaken the effects of distant transport process on surface ozone by scavenging function on ozone precursors and low solar radiation during and around rainy days (Shan et al., 2008).

4.6.1. Backward trajectory analysis

Many studies have shown that backward trajectory is a useful tool to track the transport of airmass reached at a given site (e.g., Cheung and Wang, 2001; Camalier et al., 2007). With a view to examining the effect of this on airmass trajectories, backward trajectories were computed. They have been used to investigate the origin of airmass arriving from different locations over the study region to identify the major sources responsible for the production of ozone. The airmass trajectories act as potential conduits for the transport of pollutants, were examined using the internet based HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4) was developed at the Air Resources Laboratory (ARL), National Oceanic and Atmospheric Administration (NOAA), USA (Draxler and Rolph, 2003). Fig. 10 represents 168-h (seven days) back trajectory ending at the observation site at 500 m altitude for a typical day in different months during the study period. It is clear from the airmass pathways derived from the backward trajectories, the possible transport of species from the polluted northern Indian region via the oceanic region over the Bay of Bengal before arriving the sampling site attributes possible increase in the production of ozone during the winter period. Even though they originate from land and spend half their life over the sea, when getting to the observational site, they are

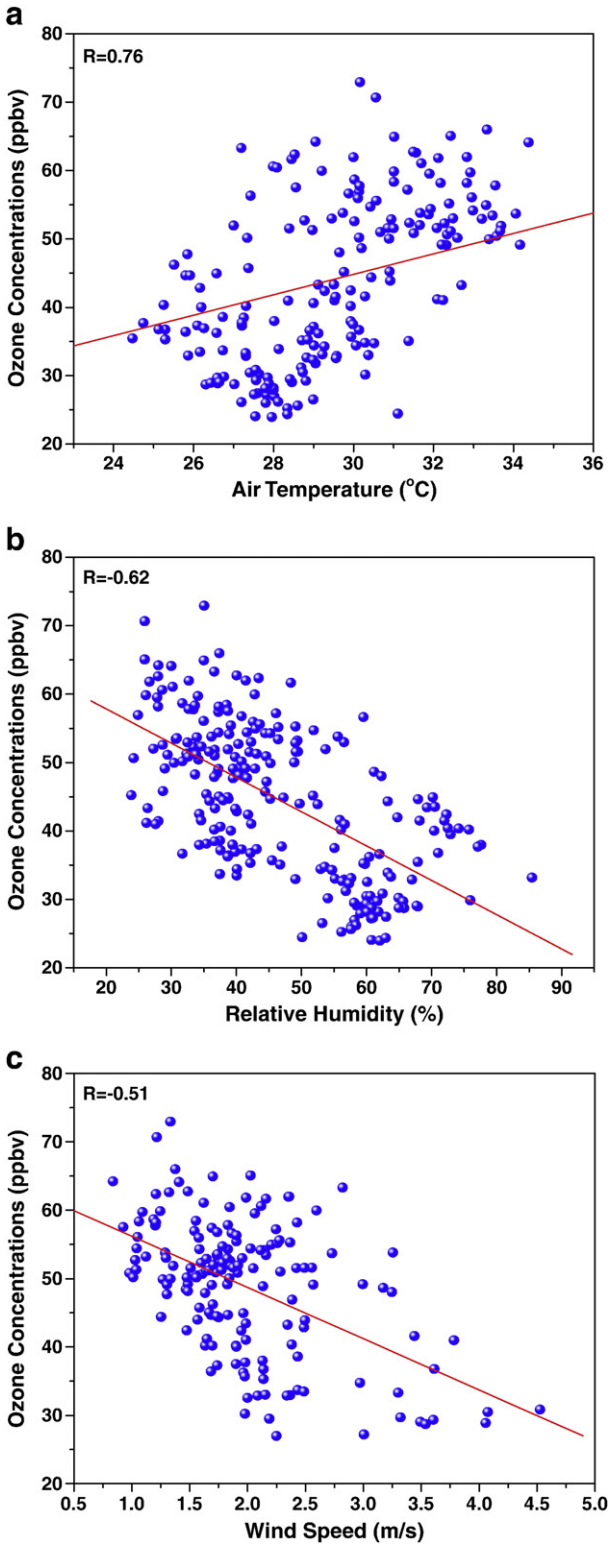


Fig. 11. Correlation between ozone concentrations versus (a) air temperature (R = 0.76, N = 184), (b) relative humidity (R = −0.62, N = 224) and (c) wind speed (R = −0.51, N = 161).

associated with high ozone concentration because they pick up the air pollutants in the highly industrialized and urbanized areas of the northern Indian region (Shan et al., 2009).

During the summer season (March–May), the airmass pathways arriving from the Arabian/African countries contribute significantly maximum ozone observed in the year because

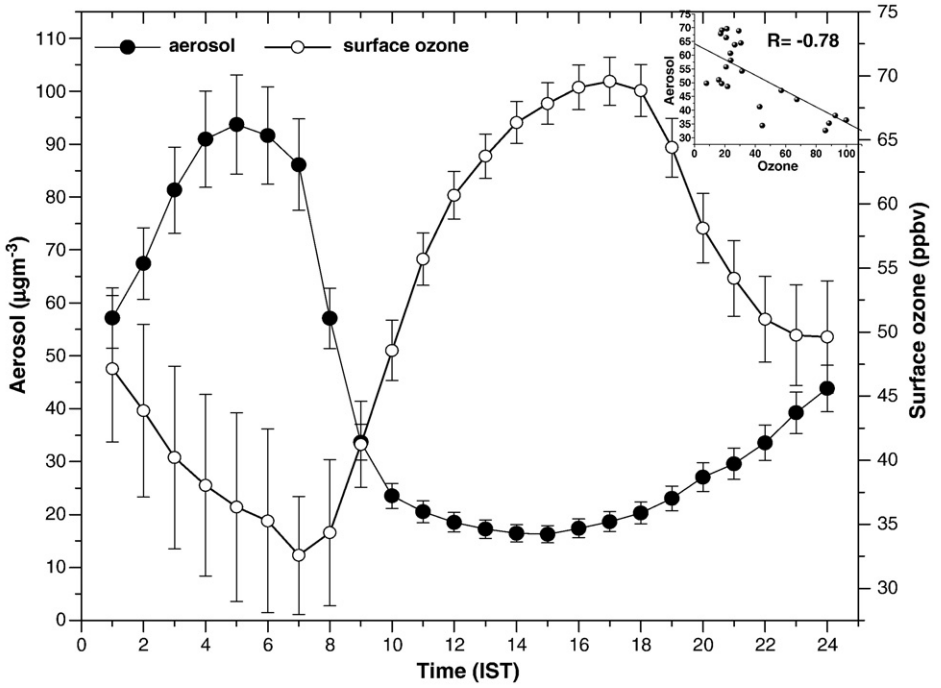


Fig. 12. Diurnal variations of hourly average concentration of ozone and aerosol during the month of March 2009. Inset figure represents the correlation between aerosol and ozone concentrations over the sampling site.

strong winds pick up desert dust from African countries at higher altitudes, which strongly correlate with the variations observed in the ozone concentration. Therefore, the increase of ozone concentration and constantly high level during summer might originate from the transport of ozone rich airmass above boundary layer associated with the elevated back ground ozone levels in India (Shan et al., 2008). Further the backward trajectory analysis shows that the highest average O_3 concentration is associated with the southeastern maritime monsoon (Tu et al., 2007). This type of airmass might cause high O_3 concentrations at this site with favorable meteorological conditions for photochemical reactions such as high temperature and low relative humidity. The high frequency of this type of airmass in East Asia contributes to common seasonal characteristics with minimum surface ozone in the summer (Xu et al., 1997; Zhang and Oanh, 2002). However, the summer minimum is not observed at this site, because the originally clean maritime airmass is polluted when passing over the highly industrialized and urbanized areas in the northern India.

The airmasses coming from the south during the monsoon season (June–July) might originate from the tropical Indian Ocean and passes over the Arabian Sea and bringing relatively somewhat pristine airmasses to the measurement site which represents low levels of ozone. This airmass also contributes to NO_2 and CO at this site. In contrast, another type of clean maritime airmass that passes over the Arabian Sea during the southwestern monsoon vague is associated with the lowest ozone concentrations because it spends a short time in the industrial and urbanized areas and a longer time in the rural areas before it reaches the measurement site. The measurement site gets more rainfall during southwest monsoon (Rao, 1976; Kumar et al., 2009b); due to rain/wash out phenomenon the airmass path is less polluted leading to low levels of ozone in monsoon.

4.6.2. Regression analysis of ozone and meteorological parameters

The correlation between O_3 concentrations and meteorological parameters like air temperature (AT), wind speed (WS), and relative humidity (RH), was also recorded at the observation site. Fig. 11a–c shows that air temperature is positively related with O_3, where as RH and WS are negatively correlated. There is a good correlation of O_3 with air temperature ($R=0.75$, $N=184$) which is shown in Fig. 11a. On the other hand, relative humidity ($R=-0.69$, $N=224$) and wind speed ($R=-0.51$, $N=161$) possess negative correlation with O_3, which plays an important role in building up of ozone concentration as shown in Fig. 11b and c, respectively. High concentrations of O_3 are therefore likely to occur with high temperature and solar radiation and low relative humidity.

4.7. Impact of aerosols on surface ozone

High aerosol concentration significantly affects chemical oxidation processes, especially through the photo-dissociation (Li et al., 2005). The change of aerosol concentrations has an important impact on the surface ozone concentration. Thus it is important to understand the sensitivity of ozone concentration to aerosol loading. Diurnal variation of hourly averaged ozone and aerosol concentrations that was measured simultaneously during March 2009 are shown in Fig. 12. Correlation between ozone and aerosol concentrations appears in a non-linear

behavior. The result shows that higher aerosol concentrations produce lower ozone concentrations. By contrast, the lower aerosol concentration leads to higher ozone concentrations. A negative correlation has been observed between ozone and aerosol concentrations during the month of March 2009 when the correlation coefficient was about −0.78 (see inset in Fig. 12). Browell et al. (1988) and Girgzdiene (1991) have also reported the similar result.

5. Summary and conclusions

1. The annual average diurnal variation of O_3 shows maximum concentration 77.2 ± 14.4 ppbv at noon and minimum 23.7 ± 3.7 ppbv in the morning with $\pm 1\sigma$ standard deviation. The average seasonal variation of ozone mixing ratios is observed to be maximum (52.05 ± 10.2 ppbv) during the summer and minimum (30.96 ± 5.7 ppbv) during the monsoon period. The monthly average high (low) O_3 56.09 ± 10.1 ppbv (27.45 ± 2.3 ppbv) at noon in March (July) is due to the possible increase in precursor gas concentration by anthropogenic activity and also due to the influence of meteorological parameters.
2. The rate of increase of surface ozone is high (2.11 ppbv/h) in March and low (0.32 ppbv/h) in July. The average rate of increase of O_3 from midnight to midday is 1–1.5 ppbv/h. Mixing ratios of ozone increase more during the morning than the ozone decreases during the evening. This type of diurnal variation in ozone with mixing ratios remaining high until the late evening has also been observed at some other rural sites. This has been attributed to slower titration of ozone by NO during late evening at rural sites. Mixing ratio of ozone starts increasing at about 07:30 h; it reaches to a maximum value at about 16:00 h and rapidly decreases after 18:00 h. The diurnal peak is rather broad, extending from 11:00 to 18:00 h.
3. The monthly average O_3 concentrations show a daytime maximum (67.13 ± 11.7 ppbv) in March and minimum (29.16 ± 1.9 ppbv) in July, and corresponding nighttime maximum (46.18 ± 9.9 ppbv) and minimum (25.15 ± 2.8 ppbv) with $\pm 1\sigma$ standard deviation. The daytime increase in ozone mixing ratio is basically due to photoxidation of precursor gases, like CO, CH_4, and other hydrocarbons in the presence of sufficient amount of NO/NO_x.
4. Ozone formation presented the weekend effect where ozone concentrations for weekend were distinctly higher than that on weekday, especially in summer. The probable cause of the weekend ozone effect is related to changes in VOC sensitivity and reduction in NO_x concentration.
5. The low ozone levels in June and July may be due to the short sunshine duration and high rainfall which is associated in these months. Throughout the study period, high ozone concentrations are mainly associated with the winds from 150.5° to 260.1°. Regression analysis shows that ozone showed a positive correlation with surface air temperature and negatively correlated with relative humidity and wind speed.
6. Backward trajectory analysis shows that, the increase of ozone concentration and the constant high level during the summer season might have originated from the transport of ozone rich airmass above the boundary layer. Transport of ozone from North India and East Asia regions might be a significant process for high ozone level during the summer and the winter seasons. On the other hand, the airmasses originating from the oceanic regions might bring relatively clean maritime airmasses to the measurement site which represents low levels of ozone.
7. High aerosol concentration has very strong impact on photochemical activities and ozone formation. The correlation between aerosol and ozone concentrations appears in a non-linear feature.

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References

Ahammed, Y.N., Reddy, R.R., Gopal, K.R., Narasimhulu, K., Basha, D.B., Reddy, L.S.S., Rao, T.V.R., 2006. Seasonal variation of surface ozone and its precursor gases during 2001–2003, measured at Anantapur (14.62°N), a semi arid site in India. Atmos. Res. 80, 151–164.

Asnani, G.C., 1993. Climatology of the tropics. Annual Report, Indian Institute of Tropical Meteorology, Pune, India 1, 100–204.

Bates, D., 1994. The effects of ozone on plants and people. In: Calvert, J. (Ed.), Chemistry of the Atmosphere: Its Impact on Global Change. Blackwell Scientific Publications, pp. 239–244.

Benjamin, M.T., Sudol, M., Vorsatz, D., Winer, A.M., 1997. A spatially and temporally resolved biogenic hydrocarbon emissions inventory for the California South coast air basin. Atmos. Environ. 31, 3087–3100.

Brasseur, G.P., Orlando, J.J., Tyndall, G.S., 1999. Atmospheric Chemistry and Global Change, 13. Oxford Univ. Press, New York, pp. 465–486.

Browell, E.V., Gregory, G.L., Harriss, R.C., Kirchhoff, V.W.J.H., 1988. Tropospheric ozone and aerosol distribution across the amazon Basin. J. Geophys. Res. 93 (D2), 1431–1451.

Camalier, L., Cox, W., Dolwick, P., 2007. The effects of meteorology on ozone in urban areas and their use in ascending ozone trends. Atmos. Environ. 41, 7127–7137.

Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manage. Assoc. 44, 881–899.

Chand, D., Lal, S., 2004. High ozone at rural site in India. Atmos. Chem. Phys. Discuss. 4, 3359–3380.

Chang, L., Miller, F.J., Ultman, J., Huang, Y., Stockstill, B.L., Grose, E., Graham, J.A., Ospital, J.J., Carpo, J.D., 1991. Alveolar epithetlial cell injuries by subcronic exposure to low concentrations of ozone correlates with cumulative exposure. Toxicol. Appl. Pharmacol. 109, 219–234.

Cheung, V.T.F., Wang, T., 2001. Observational study of ozone pollution at a rural site in the Yangtze Delta of China. Atmos. Environ. 35, 4947–4958.

Crutzen, P.J., Lawrence, M.G., Poschl, U., 1999. On the back ground photochemistry of trospheric ozone. Tellus 51, 123–146.

Debaje, S.B., Kakade, A.D., 2006. Weekend effect over rural and urban site in India. Aerosol Air Qual. Res. 6, 322–333.

Debaje, S.B., Johnson, S.J., Ganesan, K., Jadhav, D.B., Seetaramayya, S., 2003. Surface ozone measurements at tropical rural coastal station Tranquebar, India. Atmos. Environ. 37, 4911–4916.

Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

EPA (Environmental Protection Agency), 1993. Air Quality Criteria for Ozone and Related Photochemical Oxidants. EPA, Washington, DC, pp. 3–6.

Finlayson-Pitts, B., Pitts Jr., J., 1997. Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. Science 276, 1045–1051.

Fishman, J., Crutzen, P.J., 1977. A numerical study of photochemistry using a one dimensional model. J. Geophys. Res. 82, 5897–5906.
Fishman, J., Crutzen, P.J., 1978. The origin of ozone in troposphere. Nature 274, 855.
Girgzdiene, R., 1991. Surace ozone measurements in Lithuania. Atmos. Environ. 25A, 1791–1794.
Glavas, S., 1999. Surface ozone and NO_x concentrations at a high altitude Mediterranean site Greece. Atmos. Environ. 33, 3813–3820.
Hogsett, W.E., Weber, J.E., Tingey, D.T., Herstrom, A.A., Lee, E.H., Laurence, J.A., 1997. An approach for characterizing tropospheric ozone risk to forests. Environ. Manag. 21, 105–120.
Kalbokas, P.D., Repapis, C.C., 2004. A climatological study of rural surface ozone in central Greece. Atmos. Chem. Phys. 4, 1139–1147.
Kelly, N.A., Wolff, G.T., Ferman, M.A., 1984. Sources and sinks of ozone in rural areas. Atmos. Environ. 18, 1251–1266.
Kleinman, L., Lee, Y., Springston, S.T., Nunnermacker, L., Zhou, X., Brown, R., Hillock, K., Klotz, P., Leahy, D., Lee, J.H., Newman, L., 1994. Ozone formation at a rural site in the southern United States. J. Geophys. Res. 99, 3469–3482.
Kley, D., Kleinmann, M., Sanderman, H., Krupa, S., 1999. Photochemical oxidants: state of the science. Environ. Pollut. 100, 19–42.
Kumar, K.R., Narasimhulu, K., Reddy, R.R., Gopal, K.R., Reddy, L.S.S., Balakrishnaiah, G., Moorthy, K.K., Babu, S.S., 2009a. Temporal and spectral characteristics of aerosol optical depths in a semi-arid region of southern India. Sci. Total Environ. 407, 2673–2688.
Kumar, K.R., Narasimhulu, K., Balakrishnaiah, G., Reddy, B.S.K., Gopal, K.R., Reddy, R.R., Moorthy, K.K., Babu, S.S., 2009b. Size segregated mass concentration and size distribution of near surface aerosols over a tropical Indian semi-arid station, Anantapur: impact of long range transport. Sci. Total Environ. 407, 5589–5604.
Lal, S., Naja, M., Jayaraman, A., 1998. Ozone in the marine boundary layer over the tropical Indian Ocean. J. Geophys. Res. 103, 18907–18917.
Lal, S., Naja, M., Subbaraya, B.H., 2000. Seasonal variations in surface ozone and its precursors over an urban site in India. Atmos. Environ. 34, 2713–2724.
Li, G., Zhang, R., Fan, J., Tie, X., 2005. Impact of black carbon aerosol on photolysis frequencies and ozone in the Houston area. J. Geophys. Res. 110, D23206.
Lin, X., Trainer, M., Liu, S.C., 1988. On the nonlinearity of the tropospheric ozone production. J. Geophys. Res. 93, 15879–15888.
Logan, J.A., 1989. Tropospheric ozone: seasonal behavior, trend and anthropogenic influence. J. Geophys. Res. 90, 10463–10482.
Mazzeo, N.A., Venger, L.E., Chasen, H., 2005. Ananlysis of NO, NO_2, O_3 and NO_x concentrations measured at a green area of Buenos Aires city during wintertime. Atmos. Environ. 39, 3055–3068.
Nair, P.R., Chand, D., Lal, S., Naja, M., Parameswaran, K., Ravindran, S., Venkataramani, S., 2002. Temporal variations in surface ozone at Thumba (8.6°N, 77°E)- a tropical coastal site in India. Atmos. Environ. 36, 603–610.
Naja, M., Lal, S., 2002. Surface ozone and precursor gases at Gadanki (13.5°N, 79.2°E), a tropical rural site in India. J. Geophys. Res. 107. doi:10.1029/2001JD000357.
Naja, M., Lal, S., Chand, D., 2001. Diurnal and seasonal variabilities in the surface ozone at a high altitude site Mt. Abu (24.6°N, 72.7°E, 1680 masl) in India. Atmos. Environ. 103, 19015–19033.
Petron, G., Harley, P., Greenberg, J., Guenther, A., 2001. Seasonal temperature variations Influence Isoprene Emission. Geophys. Res. Lett. 28, 1707–1710.
Poisson, N., Kanakidou, M., Crutzen, P.J., 2000. Impacts of non-methane Hydrocarbons on Tropospheric chemistry and the oxidizing power of the Global Troposphere: 3-Dimensional modeling Results. J. Atmos. Chem. 36, 157–230.
Qin, Y., Tonnesen, G.S., Wang, Z., 2004. One-hour and eight-hour average ozone in the California South Coast air basin: trends in peaks values and sensitivity to precursors. Atmos. Environ. 38, 2197–2207.
Racherla, P.N., Adams, P.J., 2007. The response of surface ozone to climate change over the eastern United States. Atmos. Chem. Phys. Discuss. 7, 9867–9897.
Rao, Y.P., 1976. Southwest monsoon. IMD Monogr., vol. 1. Indian Meteorol. Dept, Delhi, p. 367.
Reddy, R.R., Gopal, K.R., Narasimhulu, K., Reddy, L.S.S., Kumar, K.R., Ahammed, Y.N., Rao, T.V.R., Azeem, P.A., 2008a. Diurnal and seasonal variabilities in suface ozone and its precursor gases at a semi arid site Anantapur (14.62 °N, 77.65 °E, 331 masl) in India. Int. J. Environ. Stud. 65 (2), 247–265.
Reddy, R.R., Gopal, K.R., Narasimhulu, K., Reddy, L.S.S., Kumar, K.R., Ahammed, Y.N., Reddy, C.V.K., 2008b. Measurements of surface ozone at semi-arid site Anantapur (14.62 °N, 77.65 °E, 331 masl) in India. J. Atmos. Chem. 59, 47–59.
Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley Publications, New York, p. 1326.
Shan, W., Yin, Y., Zhang, J., Ding, Y., 2008. Observational study of surface ozone at an urban site in East China. Atmos. Res. 89, 252–261.
Shan, W., Yin, Y., Lu, H., Liang, S., 2009. A meteorological analysis of ozone episodes using HYSPLIT model and surface data. Atmos. Res. 93, 767–776.
Shende, R.R., Jayaraman, K., Sreedharan, C.R., Tiwari, V.S., 1992. Broad Features of Surface Ozone Variations over Indian Region. Paper presented at Quadrennial Ozone Symposium, Intl. Ozone Comm., Charlottesville, VA.
Subbaraya, B.H., Lal, S., 1998. Tropospheric chemistry. PINSA 63, 277–288.
Trainer, M., Williams, E.J., Parrish, D.D., Buhr, M.P., Allwine, E.L., Westberg, H.H., Fehsenfeld, F.C., Liu, S.C., 1987. Models and observations of impacts of natural hydrocarbons on rural ozone. Nature 329, 705–707.
Tu, J., Xia, Z.G., Wang, H.S., Li, W.Q., 2007. Temporal variations in surface ozone and its precursors and meteorological effects at an urban site in China. Atmos. Res. 85, 310–337.
Varotsos, C., Caratlis, C., 1991. Re-evaluation of surface ozone over Athens, Greece for the period 1901–1940. Atmos. Res. 26, 303–310.
Varotsos, C., Kondratyev, K., Efstathiou, M., 2001. On the seasonal variation of the surface ozone in Athens, Greece. Atmos. Environ. 35, 315–320.
Vingarzan, R., Thompson, B., 2004. Temporal variations in daily concentrations of ozone and acid related substances at saturna island, British Columbia, Canada. J. Air Waste Manag. Assoc. 54, 459–472.
Volz, A., Kley, D., 1998. Evaluation of the Montsouris series of ozone measurements made in the nineteenth century. Nature 332, 240–242.
Xu, J., Zhu, Y., Li, J., 1997. Seasonal cycles of surface ozone and NO_x in Shanghai. J. Appl. Meteorol. 36, 1424–1429.
Zhang, B.N., Oanh, N.T.K., 2002. Photochemical smog pollution in the Bangkok Metropolitan Region of Thailand in relation to O_3 precursor concentrations and meteorological conditions. Atmos. Environ. 36, 4211–4222.