Surface ozone variation at Bhubaneswar and intra-corelationship study with various parameters

P S Mahapatra, J Jena, S Moharana, H Srichandan,
T Das*, G Roy Chaudhury and S N Das

CSIR – Institute of Minerals and Materials Technology, Bhubaneswar 751 013, India.
**Corresponding author. e-mail: trupti.sreyas@gmail.com truptidas@immt.res.in*

This paper summarizes the results of year long (December 2009 to January 2011) continuous measurements of daytime (0700–1745) ozone (O_3) in the ambient air and related meteorological parameters at Bhubaneswar (21°15′N–85°15′E), Odisha. The seasonal variation shows distinct daytime ozone maxima during winters with a peak in January (∼85 ppbv), a slight increase (∼38 ppbv) in June and lowest in August (∼20 ppbv). The backward trajectory analysis during winter months suggests long distance transport of airmass from mainly Indo-Gangetic Plains (IGP) and western part of Indian peninsula, a major industrial hub. In other seasons, wind reaches the observation site from less polluted landmasses and the Bay of Bengal, thereby considerably reducing the pollution load. On the contrary, ozone build-up was found to be maximum and minimum in pre-monsoon and monsoon, respectively. An anti-weekend ozone effect (∼5 ppbv) was observed in winter. Paired t-test and F-test along with principal component analysis (PCA) were done to determine significance between various components (ozone, precursors and meteorological parameters). The t- and F-test showed significant monthly variation of ozone mixing ratio. The PCA showed that three components explained 79.1% of variances.

1. Introduction

Rising Ozone mixing ratio in the troposphere has been a cause of concern due to its potential effect on the atmosphere as an oxidising agent as well as a greenhouse gas (National Research Council 1991; Mickley *et al.* 2001). As a photochemical oxidant, tropospheric ozone has an adverse effect on human health, damages the green cover and also participates in the decay of urban infrastructure (Crutzen 1974; Heck *et al.* 1982; Schutt and Cowling 1985; Woodman and Cowling 1987; Logan 1989; Hisham and Grosjean 1991; Kjaergaard *et al.* 2003). Concentration of various air pollutants varies in spatial and temporal scale depending on sources of pollution, terrain topography and meteorological conditions along with boundary layer dynamics (Cartalis and Varotsos 1994; Kumar *et al.* 2010). Season and altitude have been considered to have a profound effect on the residence time of tropospheric ozone while meteorological parameters and availability of ozone precursors control its formation and decay (Kumar *et al.* 2010). Factors like high humidity and UV-B radiation, especially in the tropics, catalyze linear production of OH radicals which in turn react with the precursor gases leading to surface ozone formation (Lal *et al.* 2000; Ghude *et al.* 2006). In general, ozone mixing ratio within the troposphere can be influenced both by various physico-chemical processes and dynamic

Keywords. Ozone; solar flux; anti-weekend effect; coastal site; statistical approach; atmospheric sciences; climate; data analysis.

processes. Downward transport of the ozone-rich air from aloft (as a result of the stratospheric intrusions), horizontal regional air pollution transfer including transcontinental transfer (Li *et al.* 2002), and convective growth of the atmospheric boundary layer are the main dynamical mechanisms which define ozone mixing ratio at a particular measuring site (Beyrich *et al* 1996a, 1996b). In this context, there have been some reports of rise in the mixing ratio of tropospheric ozone due to adequate availability of precursors like, CO, NO_X, NMHC, etc., in several mega cities as well as townships closer to the industrial area in the Indian subcontinent (Lal *et al.* 2000; Ghude *et al.* 2006, 2008; Purkait *et al.* 2009; Singla *et al.* 2011). However, there is little information regarding the surface ozone mixing ratio and its precursor gases in the state of Odisha situated in the eastern coastal part of India, where several mining, fertilizer and food processing industries along with thermal power plants have been set-up in the recent past. A methodical approach is therefore crucial to understand the chemistry of tropospheric ozone mixing ratio, particularly in the Indian subcontinent, with prevalence of increasing surface ozone mixing ratio in the current era of globalisation and free economy (Kulkarni *et al.* 2010; Singla *et al.* 2011).

Pertaining to limited observational sites in the east-coast of India, studies of rising ozone mixing ratio at Bhubaneswar would be vital in generating useful information on a regional basis for the development of an overall database *vis-à-vis* the ozone mixing ratio over the Indian subcontinent.

2. Methodology

2.1 *Observation site and general meteorology*

Bhubaneswar, an urban city, is located in the eastern belt of coastal state Odisha, in the subcontinent of India. It is the capital city and locally known as 'The Temple City' which lies between, 21°15′N and 85°15′E, at an altitude of 45 m a.s.l. Geographically, Bhubaneswar is situated in the eastern coastal plains of Odisha and south-west of the Mahanadi River having a tropical wet and dry climate. Bhubaneswar being one of the fastest developing cities in the eastern part of the country is subdivided into a number of townships and housings. Apart from urbanisation, there is sporadic growth of different industries such as cement, thermal power station, sea port, fertilizer plants producing nitrogen-based fertilisers, mining activities, metallurgical plants such as sponge iron, cement, etc., at 200 km radius of the township (figure 1). The average temperature ranges between a minimum of around 10°C in the winter to a maximum of 40°–45°C in pre-monsoon. The summer (pre-monsoon) months from March to May are hot and humid and temperatures often shoot past 40°C in May. One of the most common features of the city is the sudden afternoon thunderstorms accompanied with high wind and rain events during pre-monsoon, locally called as 'Kal Vhairavi'. The southwest monsoon reaches the city during second week of June followed by July and August months receiving the maximum rainfall, with an average of 220 mm per month. Thereafter pleasant weather conditions prevail over the city during November, December and January with occasional receipt of chilly winds from the N and NE at an average speed of 7 miles/hour during mid-December to end of January. Temperatures drop to approximately 15°C during these months. The city has a population of 837,737 (http://www.census2011.co.in/census/city/270-bhubaneswar.html) and is surrounded by small townships (approximately within 100 km) where various mining and fertilizer-based industries are operational. The nearest major metropolitan city is Kolkata, 440 km away towards north. The exact sampling site is just about 1.5 km away from National Highway dominated by vehicular emissions.

The station has distinct weather conditions during various seasons of the year like pre-monsoon (March, April, May (MAM)), monsoon (June, July, August (JJA)), post-monsoon (September, October, November (SON)) and winter (December, January, February (DJF)) and receives annually maximum solar radiation during pre-monsoon followed by post-monsoon and winter. As a part of our systematic studies on measurement of pollution load due to anthropogenic activities (Das *et al.* 2005, 2009, 2010, 2011), the focus of the present study has been analysis of ozone mixing ratio for a period (December 2009–January 2011) and correlation of the same with its precursors and other meteorological parameters.

2.2 *Ozone observation and data analysis*

Ozone mixing ratio at the station was monitored with the help of online analyzers installed on the rooftop of Institute of Minerals and Materials Technology, located in a relatively clean environment of the city. The analyzer used for measuring ozone was 'Thermo Scientific' Model 49*i* UV Photometric Ozone Analyzer which is based on the principle of UV-photometric absorption. Ambient air was collected through a Teflon tube from a level of 20 m above the ground which was sucked through the instrument at a flow rate of 1 LPM without variation through an uninterrupted power

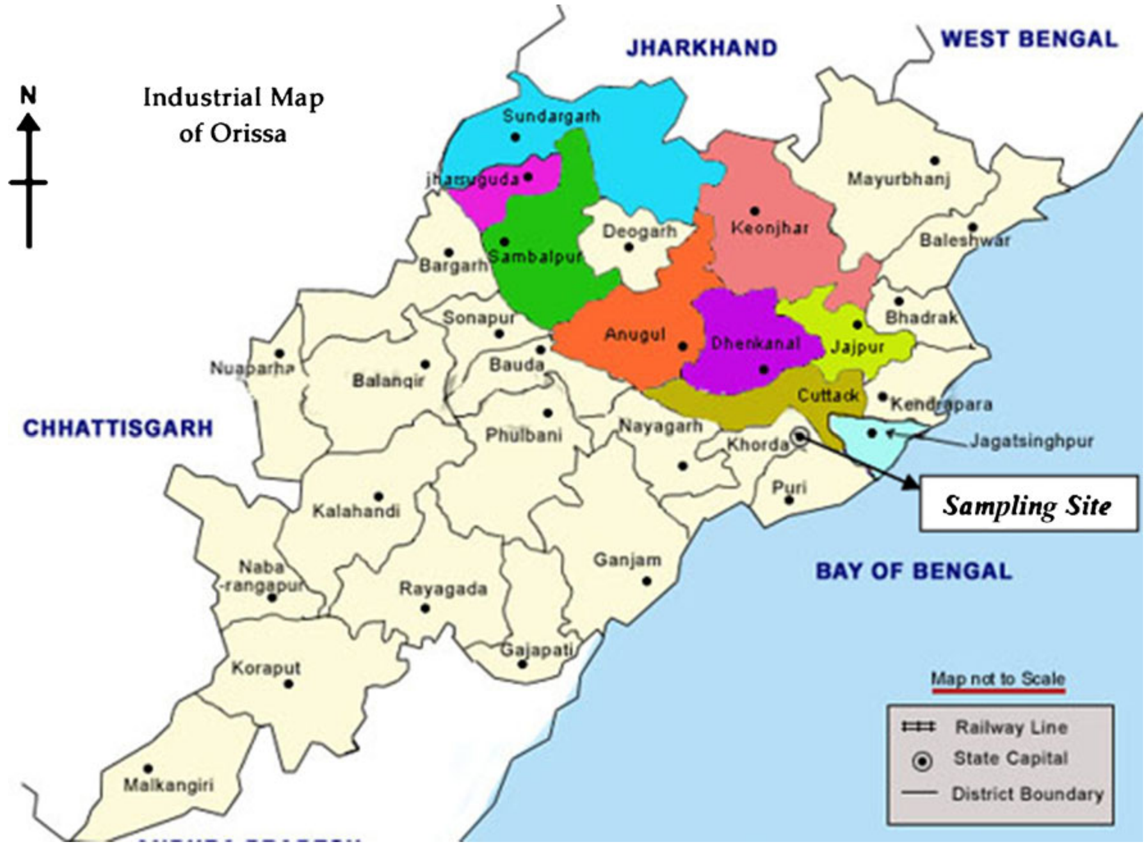

Figure 1. Industrial map of Odisha state indicating the sampling site and major industrial areas (source http://www.teamorissa.org).

source. The minimum detection limit of the analyzer is 1.0 ppbv with 20 s response time. Calibration check was performed at regular intervals to maintain the accuracy of the readings.

2.3 *Meteorological parameters and backward trajectory*

Various meteorological parameters (temperature, humidity, wind speed) were collected using AWS (model MW8001-01/04 LSI spa make) placed at the sampling location itself.

Total solar radiation (considering both direct and diffused) was measured directly by means of Pyranometer (Campbell Scientific – CR 850) within the wavelength 0.285 to 2.8 micron. It continuously collects data in every 15 minutes which is averaged for a day and then for a month.

Backward wind trajectory patterns have been traced using weekly backward trajectories at Bhubaneswar through the HYSPLIT (Hybrid Single-Particle Langrangian Integrated Trajectory) model of NOAA (Draxler and Rolph 2011) for Bhubaneswar as shown in figure 2. The station being nearer to sea (∼60 km away from the seashore) backward wind trajectories were traced at three levels, i.e., 200, 500 and 1000 m AGL, through vertical velocity model every week, during the study period. For the ease of analysis it was chosen to display a seasonal trend of backward trajectories. Five weekly data in a month and three levels of trajectories in each week were traced for three months (one season). Thus 45 trajectories were diagrammatically clubbed on the map to determine the source of wind for a particular season.

2.4 *Multivariate analysis*

Multivariate analysis and principal component analysis (PCA) were used to identify the possible emission sources of pollutants and correlations among them. Daily average values of all parameters, i.e., ozone, NO, NO_2, NO_X, temperature, humidity, wind speed and solar flux were examined for the period December 2009 to November 2010. PCA is widely used to reduce variables and to extract a small number of latent factors in order to analyze the relationships among observed variables. To make the results more easily interpretable, the PCA with VARIMAX normalized rotation was also applied, that can maximize the factor loadings through variables for each factor. In this study, all principal factors extracted from the variables with eigenvalues up to 1 were considered

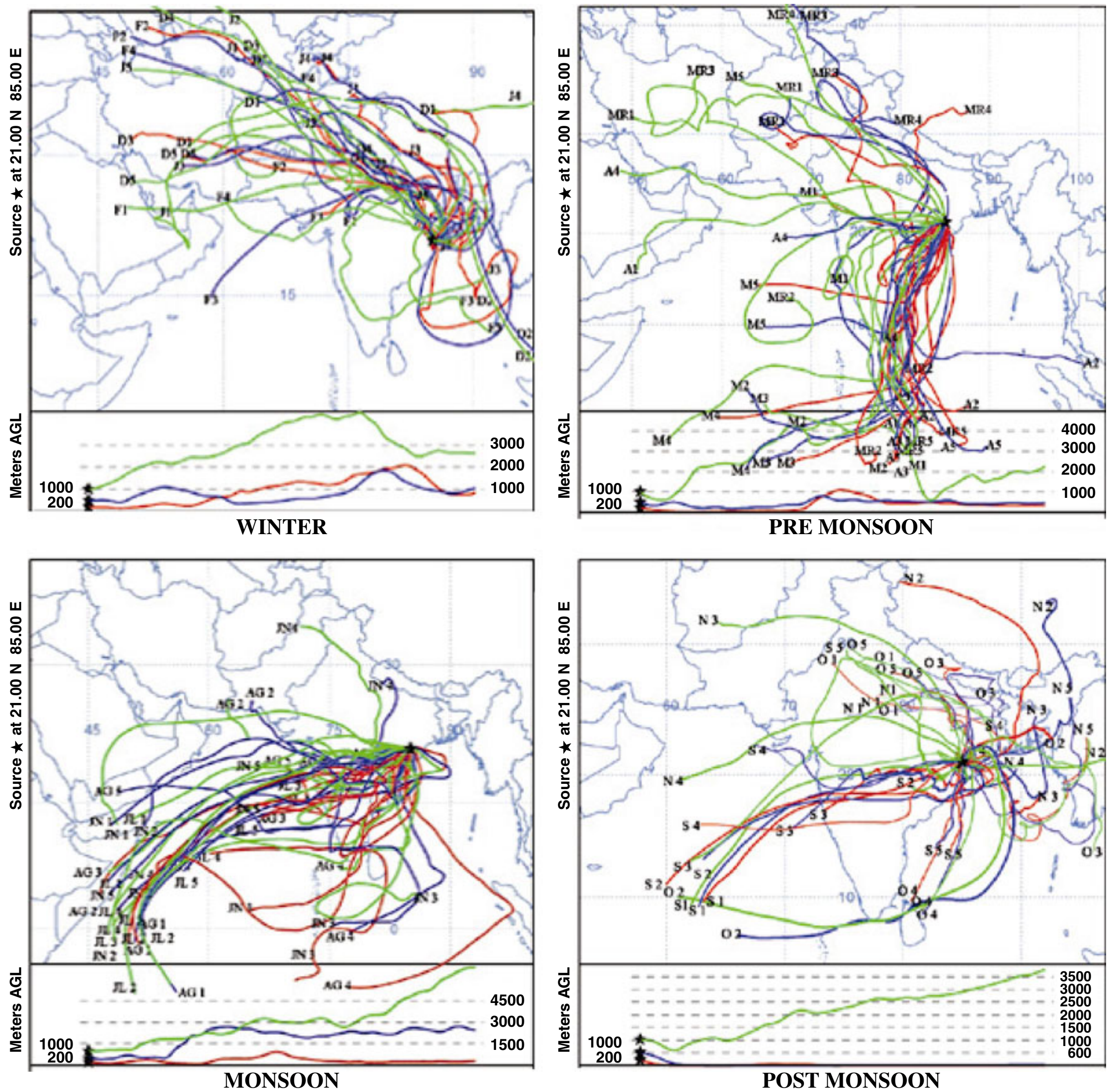

Figure 2. Wind back trajectory analysis from December 2009 to November 2010.

since the result for values ≤1 were not significant (Kim *et al.* 2009). When PCA with VARIMAX normalized rotation was performed, each PCA score contained information about all the variables combined into a single number, while the loadings indicated the relative contribution each variable makes to that score.

3. Results and discussions

3.1 *Monthly and seasonal ozone variation*

Annual variation of daytime ozone and its correlation with some meteorological parameters such as relative humidity, solar flux, wind directions, etc., were observed for the period December 2009–January 2011. The analyzer averages data for every 15 minutes interval and stores in the memory which were retrieved regularly for use in the study. The 15 minutes data (between 7:00 and 17:45 hrs) were averaged for each day to find the daytime average ozone mixing ratio, and then averages for a month were again averaged to determine the daytime monthly average ozone mixing ratio. Figure 3 shows the monthly average of daytime ozone mixing ratio from December 2009 to January 2011. It can be observed that during winter months (December 2009, January 2010 and February 2010) the daytime average ozone mixing ratio was ∼75 ppbv followed by a gradual decrease during pre-monsoon (March 2010, April 2010 and May 2010) with a daytime average ozone mixing ratio of ∼38 ppbv, ∼28 ppbv during monsoon (June–August 2010) and ∼29 ppbv (September–November 2010) during post-monsoon. The state of Odisha usually receives the first monsoon showers during the 2nd week of June, hence the months

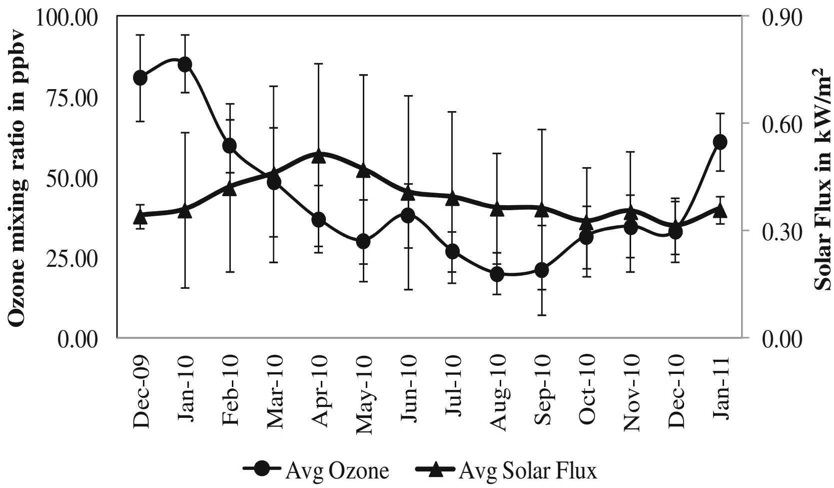

Figure 3. Average monthly variation of mean solar flux with mean ozone mixing ratio from December 2009 to January 2011.

of, June, July and August are included under the monsoon season and a lower daytime ozone mixing ratio is expected during this period. On the contrary in the month of June 2010 the average daytime ozone mixing ratio was observed to be slightly high ∼38 ppbv followed by 27 and 20 ppbv during July 2010 and August 2010, respectively. This slight rise in the daytime ozone mixing ratio observed through June 2010 might possibly be accounted to the seasonal shifts resulting in a dry monsoon period. The regular monsoons arrived during the month of July 2010. This dry monsoon period that was observed in the state during June 2010, might have provoked favourable conditions for higher ground level ozone formation. Also during the month of June 2010 airmasses at higher altitudes (1000 m), have been observed to flow from the polluted belt of western India, which might be carrying ozone precursors thus bringing about a slight increase in the ozone mixing ratio during this period.

The lowest ozone mixing ratio was recorded in the month of August 2010 (∼20 ppbv) followed by a gradual increase during the post-monsoon (September, October and November 2010). The daytime average ozone mixing ratio during post-monsoon was ∼29 ppbv.

Again, the monthly daytime average ozone mixing ratio was observed to be ∼33 ppbv in December 2010, which was unusual considering the data of December 2009. This discrepancy in the ozone mixing ratio during December 2010 might be due to several factors:

- A low-pressure created in the region during 6–13 December 2010 resulted in heavy rainfall. Table 1 shows the meteorological parameters like humidity, rainfall, temperature and solar flux for the month of December 2009 and December 2010. In December 2010, there were six and three rain and fog events respectively whereas in December 2009 there were none. The solar flux as well as the daily average temperature was low in December 2010 compared to December 2009, may be due to rain and fog events in the former. The daily average humidity was high in December 2010 compared to December 2009. All these factors might have played an important role in lowering the ozone mixing ratio in December 2010 compared to December 2009.
- The daily average wind speed was found to be high and daily average maximum temperature was found to be low during December 2010 in comparison to December 2009 (data taken through AWS installed at the site of observation).
- The sea-level pressure during December 2010 was also lower in comparison to December 2009.

All these factors were presumed to have a negative impact on the photochemical process leading to ozone formation.

Daytime ozone mixing ratio at Bhubaneswar is highest (75.67 ppbv) in winter season; compared to other seasons it is alarming because of its exceedance by 20 ppbv from CPCB norms in India (8 hrs ozone=100 μgm/m^3≡50 ppbv) (http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php). This increase of daytime ozone mixing ratio during winter may be due to lowering of atmospheric boundary layer and stable meteorological conditions which resist mixing of ozone with upper boundary layer accompanied with higher solar flux. The lower mixing ratios of ozone during peak summers (pre-monsoons) can be attributed to high intense solar radiation which tends to increase the temperature and provides an appropriate condition for air convection allowing expansion of the atmosphere. The presence of high relative humidity pertaining to its coastal location also leads to instances of rainfall (Baygi *et al.* 2010)

Table 1. *Daily average values of weather parameters (temperature, humidity, rainfall and solar flux) during December 2009 and December 2010.*

Date	2009				2010			
	Avg. temp (°C)	Avg. humidity (%)	Events	Daily avg. SF (kW/m^2)	Avg. temp (°C)	Avg. humidity	Events	Daily avg. SF (kW/m^2)
1 December	22	65		–	24	64		0.326
2 December	22	69		–	22	66		0.323
3 December	22	69		0.269	22	62		0.367
4 December	23	71		0.321	22	65		0.349
5 December	23	69		0.331	20	64	Rain	0.118
6 December	23	69		0.336	20	93	Rain	0.083
7 December	22	68		0.369	22	68	Rain	0.288
8 December	24	71		0.348	20	92	Rain	0.055
9 December	24	72		0.356	22	91		0.181
10 December	23	72		0.335	22	94	Rain	0.137
11 December	24	74		0.331	24	77	Fog	0.325
12 December	23	68		0.363	24	75		0.327
13 December	23	62		0.351	24	73	Rain	0.246
14 December	24	76	Fog	0.304	22	73		0.314
15 December	24	70	Fog	0.349	22	67		0.342
16 December	24	67	Fog	0.304	19	65		0.364
17 December	26	58		0.307	19	67		0.344
18 December	25	64		0.320	20	63		0.359
19 December	24	64		0.318	19	67		0.353
20 December	24	87		0.320	20	60		0.374
21 December	22	72		0.352	18	57		0.382
22 December	22	64		0.334	18	58		0.376
23 December	20	60		0.328	20	64		0.379
24 December	20	59		0.390	20	64		0.382
25 December	21	51		0.413	22	60		0.369
26 December	20	57		0.367	22	77		0.335
27 December	20	57		0.390	21	72	Fog	0.311
28 December	20	52		0.380	20	71	Fog	0.310
29 December	21	52		0.398	20	66		0.345
30 December	21	57		0.307	20	68		0.356
31 December	22	64		0.343	22	70		0.332

and strong wind during this season cause extended periods of instability which in turn tends to ventilate the lower troposphere (Tiwari *et al.* 2008). Also during monsoon, high rainfall causing rain wash-out effect and higher wind speed than winter accounts for lower value of ozone mixing ratio. The annual distribution of ozone at Bhubaneswar, depicting a high winter mixing ratio is in accordance with studies of different urban locations (Lal 2007) and bears a disparity with previous studies of Nair *et al.* (2002); Debaje *et al.* (2003) and Kulkarni *et al.* (2010) which suggest ozone mixing ratio to be highest during pre-monsoon and lowest during winters. An air back trajectory analysis for Bhubaneswar described in figure 2 was done so as to determine the influence of airmass on daytime ozone variation and the seasonal impacts.

The most probable back trajectory analysis for Bhubaneswar, during 2010 is shown in figure 2. The analysis explains that during the winter months airmass comes from Indo-Gangetic Plains in the two lower altitudes, i.e., 200 and 500 m. At higher altitude (1000 m), the airmass is transported from western sector of India. Western India being a major industrial hub (thermal power plant, petro chemicals and metallurgical industries) produces ample ozone precursors (NO_X, VOCs and CO). Specifically the higher altitude winds apart from bringing industrial pollutants from western India, may have a profound influence on transport of dust aerosols from Sahara and other African regions (Pathak *et al.* 2011) to Bhubaneswar. This feature also matches the source apportionment studies of aerosols done at our site by High Volume Sampler (HVS) and Ion Chromatograph (IC) which show a deep influence of acidifying agents (i.e., nitrates and sulphates) during the winter months (data to be published). Due to the above-mentioned reasons the daytime ozone mixing ratio increases considerably during winters pertaining to ample availability of precursors.

On the other hand, during pre-monsoon season the airmass both from higher and lower altitudes reaches Bhubaneswar passing through Bay of Bengal, thus increasing the marine load in the suspended particulate matter. However, in some cases, at higher altitudes (1000 m), the airmass also originate from western India thus carrying pollution load, but the ozone precursors might have been affected adversely by a profound marine influence at the observation site. Therefore during this season although solar radiation was much higher compared to all other seasons, a lower level of daytime ozone mixing ratio was observed as compared to winter.

During monsoon season, long range transportation was observed mainly from the Arabian Sea although a clear pattern was not visible because in some cases trajectories also originated from Bay of Bengal. Though source apportion studies were done at our sampling site (data to be published), it was observed that suspended particulate matter comprised of both marine as well as anthropogenic pollutants. However, coupled with lower solar flux due to cloudy sky and washing effect due to rainfall, the ozone mixing ratio was found to be least.

The post-monsoon wind trajectories also do not have a definite trend as in the monsoon season. At higher altitudes, the airmasses either originated from Arabian Sea, Bay of Bengal or western part of India and at lower altitudes mostly trajectories originated from the Arabian Sea or Bay of Bengal. Therefore, the suspended particulate matter consisted of both marine as well as anthropogenic pollutants.

3.2 *Variation of ozone mixing ratio with solar flux and ozone build-up*

3.2.1 *Variation of ozone mixing ratio with solar flux*

A comparative analysis of mean solar flux and mean daytime ozone mixing ratio in the atmosphere during the study period is shown in figure 3. It was observed that during peak summer periods, with increase in solar flux, there had been a marked decrease in the mixing ratio of ozone. However, for the rest of the year the solar flux has mostly remained constant and ozone has followed a normal seasonal trend. A possible reason for this unusual behaviour of decrease in daytime ozone mixing ratio during peak summers (when the solar flux is maximum) can be accounted to the instability conditions (that hampers the photochemical reaction due to lesser accumulation of precursors) prevailing in the atmosphere during the study period. The observation site experiences a frequent windy and stormy condition during afternoons in the pre-monsoon season locally termed as 'Kal Vhairavi', which might be creating instability and turbulent weather conditions rendering low daytime ozone mixing ratio (Kritz *et al.* 1990). Another reason could be the simultaneous expansion of the boundary layer with increase in temperature during summer, thus increasing the volume of the atmosphere, leading to dilution in the concentration of surface ozone as well as its precursors. Section 3.1 can be referred for further clarification regarding the same with respect to airmass flow during pre-monsoon.

3.2.2 *Ozone build-up on high and low insolation day analysis*

Photochemical ozone build-up for the period of December 2009 to January 2011 has been shown in figure 4. The build-up in various seasons has been determined by considering the difference between the daily average ozone concentration during high and low insolation days ascertained from 50 % and 25 % of days in the respective months (during December 2009–January 2011) with the highest and lowest solar radiation, respectively (Kumar *et al.* 2010). Annual average ozone on high insolation days was estimated to be 50.82 ppbv whereas that on low insolation days was 28.63 ppbv, while the annual average ozone build-up was found to be 22 ppbv. Ozone build-up showed maxima during pre-monsoon followed by winter, post-monsoon and monsoon. It has been observed (figure 1) that the location receives maximum solar flux during pre-monsoon (0.48 kW/m^2) followed by winter (0.37 kW/m^2), post-monsoon (0.35 kW/m^2) and monsoon (0.39 kW/m^2). Due to delay in onset of monsoon, associated with clear sky and low surface wind, the average solar flux in monsoon months is somewhat higher as compared to post-monsoon. Apparently higher insolation (solar flux) in pre-monsoon catalyzes the formation of higher ozone mixing ratio. However, as discussed in section 2.1, the observation site being apparently closer to the sea shore ($\sim$60 km away), experiences occasional rain and thunderstorm events along with high intensity of wind movements, especially in the afternoon during pre-monsoon. Such phenomenon brings about a decline in ozone mixing ratio resulting in an increase in the difference between the mixing ratio, during high and low insolation days. This could be one of the reasons of detection of high ozone build up during pre-monsoon, even when the daily average ozone mixing ratio was lower in comparison to winter.

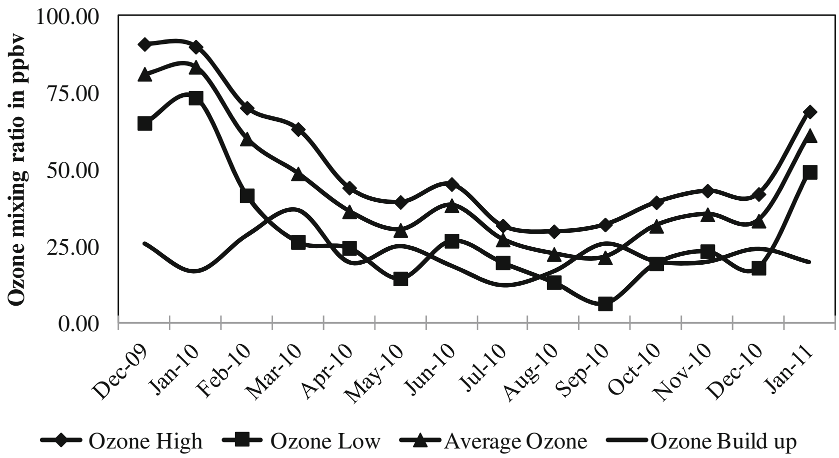

Figure 4. Monthly ozone build-up from December 2009 to January 2011.

3.3 *Diurnal variation*

The diurnal variation pattern of ozone at Bhubaneswar is shown in figure 4. Ozone a secondary pollutant can be formed at any instance of time with the availability of sufficient ozone precursors and daylight (Pulikesi *et al.* 2006). Followed by sunrise, ozone begins to form from its precursor trace gasses due to photochemical reaction. Therefore, the ozone mixing ratio values were found to increase with sunrise and was highest between 10:30 am and 14:00 pm due to peak solar flux during this period and thereafter there was a dip pertaining to gradual decrease in solar radiation. Such kind of a diurnal pattern characterized by maximum ozone mixing ratio in the afternoon and low levels during late night and lowest during early morning hours is at par with previous studies (Nair *et al.* 2002; Debaje *et al.* 2003; Tu *et al.* 2007; Nishanth and Satheesh 2010).

The seasonal diurnal pattern has been determined by taking the overall average of the diurnal ozone mixing ratio of various months. It could be observed that the pattern is almost similar in all the seasons with a rise in ozone mixing ratio after sunrise further attaining highest value during noon. However, it can be clearly observed that there was a significant difference in the average ozone mixing ratio values for various seasons. During winters the diurnal pattern showed peak ozone mixing ratio values followed by pre-monsoon and almost similar values during monsoon and post-monsoon periods. Such behaviour could be expected due to its direct relationship to the availability of precursor gases and favourable meteorological conditions (figure 5).

3.4 *Weekend and weekday ozone analysis*

Weekends and weekdays ozone mixing ratio analysis was carried out at this sampling site. Normally an ozone high weekend effect is quite evidently observed at various urban locations, not only in India but also worldwide (Qin *et al.* 2004; Pudasaineea *et al.* 2006; Debaje and Kakade 2006; Shan *et al.* 2008; Schipa *et al.* 2009). However, our analysis depicts that during the months of November, December and January on weekdays the ozone mixing ratio was found to be higher through an average margin of ∼5 ppbv suggesting an anti-weekend ozone effect. However, during February to October, variation of ozone mixing ratio between weekdays and weekends was not observed. Based on the observational data, the characteristics of weekend and weekday surface ozone variation with seasons were investigated. The probable cause of anti-weekend effect at this location during peak winters could be accounted to the presence of high concentration of ozone precursors (NO_X) (through vehicular emissions mostly and certain industrial emissions from nearby areas) assisted with an evident stable atmospheric condition prohibiting mixing and transport, thus generating high amount of ozone precursors on weekdays that ultimately contributes to higher ozone mixing ratio during weekdays and *vice versa*.

3.5 *Statistical studies*

3.5.1 *Significance of variation of ozone mixing ratio by f- and student t-test*

Two-way Analysis of Variance (ANOVA) was used to determine whether monthly average values of daytime ozone mixing ratio has any significant variation or not datewise and month/seasonwise for the period of December 2009 to November 2010. In order to determine the same we have used the null hypothesis technique. Null hypothesis assumes that there is no variation monthly/seasonal and datewise average O_3 mixing ratio. So if F value

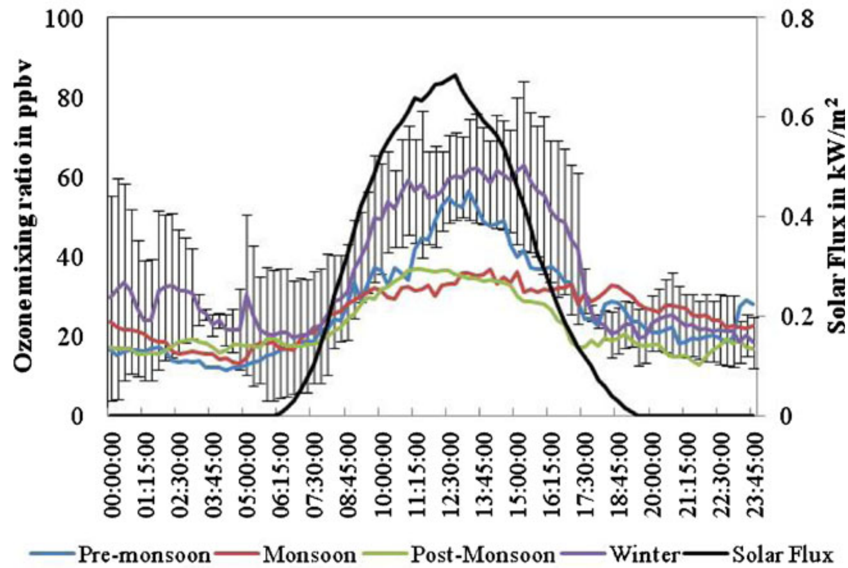

Figure 5. Variation of seasonal average diurnal ozone mixing ratio with annual average diurnal solar flux.

(calculated) is less than or equal to critical values then it is assumed that there is no variation (Gupta 2005). On the contrary if the F-calculated value is more than F-critical then the null hypothesis does not hold good, i.e., there is significant variation in daytime ozone mixing ratio. The F-critical and calculated values are shown in table 2. Based on the F (critical and calculated) values p-values were determined which indicates the confidence level. In the present case, the F-critical value is based on 95% confidence level ($p < 0.05$). The p value in table 2 shows that the confidence level is more than 95% where the results were significant. It was observed that both seasonwise and yearwise, the ozone mixing ratio varied significantly as F-calculated value is more than critical. Further datewise analyses showed that the variation is not significant except in post-monsoon period. To determine the robustness of this study, student t-test was carried out to ascertain the significance of variation in monthly ozone mixing ratio. The results are shown in table 3. Except for December 2009–January 2010 all other months showed significant variation. The non-significant values for December 2009 and January 2010 through t-test clearly indicate a similarity in ozone mixing ratio

Table 2. *Two-way ANOVA analyses for O_3 mixing ratio at $p = 0.05$. Where DJF is December 2009, January 2010, February 2010; MAM is March 2010, April 2010, May 2010; JJA is June 2010, July 2010, August 2010; SON is September 2010, October 2010, November 2010.*

Period	F-observed	p-value	F-critical	Remarks
Annual				
Datewise	1.22	0.25	1.68	Non-significant
Monthwise	95.60	0.00	1.84	Significant
Seasonwise				
DJF				
Datewise	1.17	0.32	1.77	Non-significant
Monthwise	31.93	0.00	3.20	Significant
MAM				
Datewise	0.97	0.51	1.93	Non-significant
Monthwise	14.39	0.00	3.28	Significant
JJA				
Datewise	1.08	0.40	1.73	Non-significant
Monthwise	35.63	0.00	3.18	Significant
SON				
Datewise	2.80	0.00	1.69	Significant
Monthwise	21.66	0.00	3.17	Significant

Table 3. *Comparison of significance between the months ozone mixing ratio region using paired t-test at $p = 0.05$.*

Season	Values		Remarks
	t-critical	t-observed	
Winter			
December 2009 and January 2010	1.71	0.00	Non-significant
January 2010 and February 2010	1.71	7.76	Significant
December 2009 and February 2010	1.70	5.79	Significant
Pre-monsoon			
March 2010 and April 2010	1.70	3.89	Significant
April 2010 and May 2010	1.74	2.66	Significant
March 2010 and May 2010	1.74	5.63	Significant
Monsoon			
June 2010 and July 2010	1.71	4.82	Significant
July 2010 and August 2010	1.70	5.59	Significant
June 2010 and August 2010	1.71	7.08	Significant
Post-monsoon			
September 2010 and October 2010	1.70	4.16	Significant
October 2010 and November 2010	1.70	2.37	Significant
September 2010 and November 2010	1.70	6.12	Significant

Table 4. *Corelationship of ozone, other pollutant load and meteorological parameters.*

	Ozone	NO	NO_2	NO_X	Days	Avg. temperature	Avg. humidity	Wind speed	Solar flux
Ozone	1.00								
NO	0.11	1.00							
NO_2	−0.12	**0.33**	1.00						
NO_X	−0.02	**0.81**	**0.81**	1.00					
Days	**−0.68**	0.01	**0.35**	0.23	1.00				
Average temperature	**−0.54**	−0.18	−0.11	−0.18	**0.30**	1.00			
Average humidity	**−0.62**	0.02	**0.37**	0.24	**0.68**	0.17	1.00		
Wind speed	**−0.30**	−0.12	−0.29	−0.25	0.03	**0.57**	0.01	1.00	
Solar flux	0.19	−0.06	−0.24	−0.18	−0.29	**0.34**	**−0.65**	**0.30**	1.00

Bold: $p < 0.01$.

for both the months. However, this ratio is statistically different, in the month of February 2010 compared to the above months, establishing a significant variance in F-test.

3.5.2 *Determination of co-relationship and principal component analysis co-relationship matrix*

The results of correlation matrix are shown in table 4 where bold values indicate $p < 0.01$. It can be observed from the matrix that daily average ozone mixing ratio had a negative correlation with variables like days (365 days of observation), temperature, relative humidity and wind speed. As the ozone mixing ratio is based on daytime average whereas temperature and relative humidity are based on 24 hr average, a negative correlation between the variables is apparent. A positive correlation was observed between precursors, i.e., NO, NO_2 and NO_X, indicating an interdependence between the variables. The negative correlation with respect to wind speed and solar flux suggested the depletion of NO_2. Days are well correlated with average temperature and humidity suggesting that both the parameters increase with days. Average temperature shows positive correlation with solar flux and wind speed which indicates that with increase in temperature both wind speed and solar flux would show a progressive increase. Average humidity showed a negative correlation with solar flux indicating decrease in humidity with increase in solar flux.

3.5.3 *Principal component analysis*

Principal component analysis (PCA) is basically a data reduction technique for large number and

Table 5. *Rotated component matrix.*

	Component		
	1	2	3
Ozone	−0.79		
NO		0.86	
NO_2		0.74	
NO_X		0.98	
Days	0.83		
Average temperature			0.85
Average humidity	0.92		
Wind speed			0.79
Solar flux	−0.62		0.63
Eigenvalues	3.07	2.56	1.49
% Cum variance	34.11	62.56	79.10

variety of data. In the present study O_3, NO, NO_2, NO_X, days, average temperature, humidity, wind speed and solar flux are considered to be the variables. These variables are further classified into different compartments or cluster, based on the eigenvalues as shown in table 5. Component-1 comprises of factors like days, ozone, solar flux and humidity which accounted for a cumulative variance of 34.11% with eigenvalue of 3.07. Of all the factors under consideration in Component-1, ozone and solar flux showed a negative correlation with the rest and a positive correlation amongst each other, signifying the importance of photochemical reactions in surface ozone formation. Component-1 is termed as 'ozone factor' as it considers various aspects of ozone formation. Component-2 having an eigenvalue of 2.56 accounts for 62.56% of cumulative variance. It consists of variables like NO, NO_2 and NO_X having a positive correlation, suggesting that with increase in one variable the other would also increase progressively. These three variables regarded as precursors, play a vital role in determining the atmospheric ozone mixing ratio, hence Component-2 has been termed as 'precursor'. Component-3 accounts for 17.54% of variable with total cumulative variable of 79.1%. Component-3 consists of meteorological parameters like average temperature, wind speed and solar flux that have profound influence on the ozone mixing ratio. Hence the same has been termed as 'meteorological'.

4. Conclusions

An extensive study of daytime ozone mixing ratio and relevant meteorological parameters along with statistical analysis was undertaken to determine the relationship between meteorological changes, precursor concentrations and ambient ozone mixing ratio at Bhubaneswar. All the above factors along with the primary pollutants have been observed to bear a strong impact on the overall daytime ozone mixing ratio in this region. Besides normal features, a set of unique findings were observed through the study.

- The study reveals an exclusive finding regarding peak daytime ozone mixing ratio. It was found to be high during the winter months with highest mixing ratio during January ∼85 ppbv.
- The backward wind trajectories showed that during winter months especially, there is a strong flow of airmass from the polluted Indo-Gangetic Plain and western regions of India towards this region of the eastern belt. This can also be considered as a possible cause of higher daytime surface ozone mixing ratio over this region during the season.
- An ozone 'anti-weekend effect' was observed during winters with an average difference of ∼5 ppbv.
- Ozone build-up was calculated to be highest (∼27 ppbv) during pre-monsoon as compared to annual average of ∼22 ppbv.
- ANOVA and student t-test showed that monthwise variation of daytime ozone mixing ratio was significant.
- Correlation studies explicate the intra-correlation between different parameters associated with ozone variation. Simultaneously PCA showed that all the variables/parameters could be classified under three components (Component 1: ozone factor, Component 2: precursor factor, Component 3: meteorological factor) explaining 79.1% of variables.

Acknowledgements

The authors are thankful to the Director, Institute of Minerals and Materials Technology (CSIR-IMMT) and the Head, Environment and Sustainability Department (CSIR-IMMT) for their encouragement. Financial support by ISRO-GBP is gratefully acknowledged. They also acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication. The authors highly acknowledge the two anonymous reviewers for their valuable suggestions which helped to improve the manuscript.

References

Baygi M M, Ashraf B and Miyanabady A 2010 The investigation of Tehran's heat island by using the surface ozone and temperature data; *Int. J. Appl. Environ. Sci.* **5(2)** 189–200.

Beyrich F, Acker K, Kalas D, Klemm O, Moller D, Eschaller E, Werhahn J and Weisensee U 1996a Boundary layer structure and photochemical pollution in the Harz Mountains – an observational study; *Atmos. Environ.* **30** 1271–1281.

Beyrich Fr, Weisensee U, Sprung D and Gusten H 1996b Comparative analysis of sodar and ozone profile measurements in a complex structured boundary layer and implications for mixing height estimation; *Bound.-Layer Met.* **81** 1–9.

Cartalis C and Varotsos C 1994 Surface ozone in Athens, Greece, at the beginning and at the end of the 20th-century; *Atmos. Environ.* **28** 3–8.

Crutzen P J 1974 Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air; *Tellus* **26** 48–57.

Das N, Baral S S, Sahoo S K, Mohapatra R K, Ramulu T S, Das S N and Chaudhury G R 2009 Aerosol physical characteristics at Bhubaneswar, east coast of India; *Atmos. Res.* **93** 897–901.

Das N, Das R, Chaudhury G R and Das S N 2010 Chemical composition of precipitation at background level; *Atmos. Res.* **95** 108–113.

Das N, Das R, Das S N, Swamy Y V, Roy Chaudhury G and Baral S S 2011 Comparative study of chemical composition of particulate matter between sea and remote location of eastern part of India; *Atmos. Res.* **99** 337–343.

Das R, Das S N and Misra V N 2005 Chemical composition of rain water and dust fall at Bhubaneshwar in the east coast of India; *Atmos. Environ.* **39** 5908–5916.

Debaje S B and Kakade A D 2006 Weekend ozone effect over rural and urban site in India; *Aerosol and Air Qual. Res.* **6(3)** 322–333.

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

Draxler R R and Rolph G D 2011 HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD.

Ghude S D, Jain S L, Arya B C, Beig G, Ahammed Y N, Kumar A and Tyagi B 2008 Ozone in ambient air at a tropical megacity, Delhi: Characteristics, trends and cumulative ozone exposure indices; *J. Atmos. Chem.* **60** 237–252.

Ghude S D, Jain S L, Arya B C, Kulkarni P S, Kumar A and Ahmed N 2006 Temporal and spatial variability of surface ozone at Delhi and Antartica; *Int. J. Climatol.* **26** 2227–2242.

Gupta S P 2005 *Statistical Method*; Sultan Chand & Sons.

Heck W W, Taylor O C, Adams R, Bingham G, Miller J, Preston E and Weinstein L 1982 Assessment of crop loss from ozone; *J. Air Pollut. Control Assoc.* **32** 353–361.

Hisham M W M and Grosjean D 1991 Sulfur dioxide, hydrogen sulfide, total reduced sulfur, chlorinated hydrocarbons and photochemical oxidants in Southern California museums; *Atmos. Environ.* **25** 1497–1505.

Kim D J, Pradhan D, Roy Chaudhury G, Ahn J W and Lee S W 2009 Bioleaching of complex sulfides concentrate and correlation of leaching parameters using multivariate data analysis technique; *Mater. Trans.* **50** 2318–2322.

Kjaergaard S K, Pedersen O F, Miller M R, Rasmussen T R, Hansen J C and Molhave L 2003 Ozone exposure decreases the effect of a deep inhalation on forced expiratory flow in normal subjects; *J. Appl. Physiol.* **96** 1651–1657.

Kritz M A, Roulley J C L and Danielsen E F 1990 The China Clipper-fast advective transport of radon-rich air from the Asian boundary layer to the upper troposphere near California; *Tellus* **B 42** 46–61.

Kulkarni P S, Ghude S D and Bortoli D 2010 Tropospheric ozone (TOR) trend over three major inland Indian cities: Delhi, Hyderabad and Bangalore; *Ann. Geophys.* **28** 1879–1885.

Kumar R, Naja M, Venkataramani S and Wild O 2010 Variations in surface ozone at Nainital: A high altitude site in the central Himalayas; *J. Geophys. Res.* **115(D)** 16302, doi: 10.1029/2009JD013715.

Lal S 2007 Trace gases over the India region; *Indian J. Radio Space Phys.* **36** 556–570.

Lal S, Naja M and Subbaraya B H 2000 Seasonal variation in surface ozone and its precursors over an urban site in India; *Atmos. Environ.* **34** 2713–2724.

Li Q, Jacob D J, Bey I, Palmer P I, Duncan B M, Field B D, Martin R V, Fiore A M, Yantosca R M, Parrish D D, Simmonds P G and Oltmans S J 2002 Transatlantic transport of pollution and its effects on surface ozone in Europe and North America; *J. Geophys. Res.* **107(D13)** 4166, doi: 10.1029/2001JD001422.

Logan J A 1989 Ozone in rural areas of the United States; *J. Geophys. Res.* **94** 8511–8532.

Mickley L J, Murti P P, Jacob D J, Logan J A, Koch D M and Rind D 2001 Radiative forcing from tropospheric ozone calculated with a unified chemistry-climate model; *J. Geophys. Res.* **104** 30,153–30,172.

Nair P R, Chand D, Lal S, Modh K S, Naja M, Parameswaran K, Ravindran S and 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.

National Research Council 1991 Rethinking the Ozone Problem in Urban and Regional Air Pollution; National Academy Press, Washington DC.

Nishanth T and Satheesh K M K 2010 Measurement of surface ozone and its precursor NO_x over urban and rural locations in Kannur – a tropical coastal site in India; *Indian J. Sci. Technol.* **3(12)** 1198–1201.

Pathak B, Bhuyan PK, Gogoi M and Bhuyan K 2011 Seasonal heterogeneity in aerosol types over Dibrugarh-Northeastern India; *Atmos. Environ.* **47** 307–315, doi: 10.1016/j.atmosenv.2011.10.061.

Pudasaineea D, Sapkotab B, Shrestha M L, Kagac A, Kondoc A and Inoue Y 2006 Ground level ozone concentrations and its association with NO_x and meteorological parameters in Kathmandu valley; *Nepal Atmos. Environ.* **40** 8081–8087.

Pulikesi M, Baskaralingam P, Rayudu V N, Elango D, Ramamurthi V and Sivanesan S 2006 Surface ozone measurements at urban coastal site Chennai, in India; *J. Hazard. Mater.* **B137** 1554–1559.

Purkait N N, De S, Sen S and Chakraborty D K 2009 Surface ozone and its precursors at two cities in the north east coast of India; *Indian J. Radio Space Phys.* **38** 86–97.

Qin Y, Tonnesen G S and Wang Z 2004 Weekend/Weekday differences of ozone, NO_X, CO, VOCs, PM10 and the light scattering during ozone season in southern California; *Atmos. Environ.* **32** 3069–3087.

Schipa I, Tanzarella A and Mangia C 2009 Differences between weekend and weekday ozone levels over rural and urban sites in southern Italy; *Environ. Monit. Assess.* **156** 509–523.

Schutt P and Cowling E B 1985 Waldsterben a general decline of forests in Central Europe: Symptoms, development, and possible causes; *Plant Disease* **69** 548–558.

Shan W, Yin Y, Zhang J and Ding Y 2008 Observational study of surface ozone at an urban site in East China; *Atmos. Res.* **89(3)** 252–251.

Singla V, Satsangi A, Pachauri T, Lakhani A and Maharaj Kumari K 2011 Ozone formation and destruction at a sub-urban site in north central region of India; *Atmos. Res.* **101** 373–385.

Tiwari S, Rai R and Agrawal M 2008 Annual and seasonal variations in tropospheric ozone concentrations around Varanasi; *Int. J. Remote Sens.* **29(15)** 4499–4514.

Tu J, Xia Z, Wang H and Li W 2007 Temporal variations in surface ozone and its precursors and meteorological effects at an urban site in China; *Atmos. Res.* **85(3–4)** 310–337.

Woodman J N and Cowling E B 1987 Airborne chemicals and forest health; *Environ. Sci. Technol.* **21(2)** 120–126.

http://www.ucar.edu/learn/1_7_1.htm last assessed on 27th May, 2011.

http://www.census2011.co.in/census/city/270-bhubaneswar.html last assessed on 19th Jan, 2012.

http://www.teamorissa.org/MapsAndGuides.asp last assessed on 20th April, 2012.

MS received 3 November 2011; revised 18 May 2012; accepted 20 May 2012