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Summer time variation and unexpected nocturnal peak in precursors related Surface ozone concentration in air over a tropical coastal regionof Southern Tamil Nadu, India

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Abstract: Surface ozone (Surface O_3)is a secondary pollutant and there are only limited studies on ozone in South India. Studies have revealed a strong correlation between higher ozone levels and warmer days. Surface O_3 along with its precursors like NO_2, CO and CH_4 are being measured at Kanyakumari (8.0780° N, 77.5410° E), TamilNadu, India and in this paper we present the summer time variation of ozone from 2010to 2014 . Surface O_3 showed a clear diurnal variation, but an irregularity was observed during the night time for all the measuring days of Summer 2014.There was a formation of a well pronounced secondary peak in Surface O_3 during 0230 hrs accompanied by relatively strong wind patterns. Since the normal diurnal variation cannot explain this phenomenon,this uncertain behavior is probably attributed tolow NO_X titrations and the downward mixing of ozone in the ground layer.The daily mean of Surface O_3showed an increasing trend in the study area during the summer monthsand a negative correlation was observed with its precursors. The correlation of Surface O_3 with temperature and wind speed for the entire summer season was found as r= +0.68, p= 4.314E-05 and r= +0.63, p<0.0001 respectively. This linear relation in the study area is mainly due to the sea-land wind transport.A clear weekend effect was noticed for the summer months of 2013 and 2014.

Keywords: correlation, diurnal,Kanyakumari,pollutant,precursor.

INTRODUCTION

Stratospheric ozone prevents the hazardous UV from reaching our planet and is hence called good ozone. Tropospheric ozone, which is also known as ground level ozone (GLO) or Surface O_3, is very harmful and is aless known secondary pollutant. Ozone in the lower atmosphere, particularly surface ozone is highly variable in space and time (Xu et al.,2015).In humans, high ozone levels damage lung function and cause irritation to the respiratory tract by destructing the bronchioles and alveoli, leading to everlasting damage with repeated exposure (U.S EPA, 2003). The degree of adverse respiratory effects caused by ozone depends on many factors, including concentration and duration of exposure, climate characteristics, personal sensitivity, respiratory disease, and socioeconomic status (White, 1994).

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Ozone is both phytotoxic and cytotoxic. It is an important air quality issue and causes serious health problems and damage to materials and ecosystems (De Leeuw, 2000). It is now clearly established that ozone at the ambient concentrations can cause a range of effects including visible leaf damage, growth and yield reductions, and altered sensitivity to biotic and abiotic stresses (Jager, 1993). Ozone can cause significant effects on tree growth and rates of photosynthesis. Thus, elevated concentrations of O_3 can have negative impacts on human health.Primary and secondary National Ambient Air Quality Standards (NAAQS) for O_3 was established to safeguard public health and public welfare (McDonald-Buller et al., 2011). There are currently 227 counties, home to 123 million people, classified as not having attained the 75 ppb standard (www.epa.gov/airquality/greenbook/index.html). In 2015, EPA lowered the standard from 75 to 70 ppb. As the O_3 standard is varying, to precisely determine the background O_3 levels becomes more vital.

There are only limited studies on Surface O_3over southern parts of India especially in Tamil Nadu.This study intends to analyze the summer time variation ofSurface O_3 and related precursors over Kanyakumari, TamilNadu, South India. Ozone variation in summer season alone was chosen for analysis because the summer days are with high solar flux, high temperature and clear skies with less rainfall. These factors leadthe summer season to produce and hold more Surface O_3 concentration.

PRODUCTION OF SURFACE O_3 FROM PRECURSORS

Ozone is a less known pollutant formed by complex photochemical reactions of primary pollutants known as precursors in the presence of sunlight. The primary precursor of ozone is nitrogen dioxide. Deep convection and exchange events from stratosphere to troposphere can also bring down ozone-rich air from above and influence local surface ozone concentration (Jia et al., 2015; Ma et al., 2014).

$$NO_2 + h\nu\ (\lambda <= 430nm) \longrightarrow NO + O\ (^3P)$$

STUDY AREA

Kanyakumari district has atotal geographical area of 17,672 sq.Km. The District is followed by Tirunelveli District.Kanyakumari is the place where the three seas (the Indian Ocean, Arabian Sea and Bay of Bengal) meet. The District has a comfortable weather condition, which is appropriate for growing a number of crops. The nearness of the equator, its landscape and other climate factors favor the growth of various crops. Unlike other districts in Tamil Nadu, it receives rainfall both during the South West and the North East monsoons. The town has witnessed its summer season from March to May followed by southwest monsoon that extends from June to September. Northeast monsoon extends from October to December and winter season between January and February. Figure 1 shows the study area.Themean summer temperature is around 32°C and average annual rainfall is 1476 mm.The humidity and temperature of this place remain comparatively high all through the year. The site was located around one kilometre from the beach and has the influenceof strong wind patterns.

METHODS

The ozone concentration measurements were carried out by using a portable ozone monitor series 200 and 500 from Aeroqual with different heads for Nitrogen dioxide, Carbon monoxide and Methane measurements for a period of four years from 2010 to 2014. The monitor consistsof two main components, a series 200 or 500 monitor and a sensor head. Sensor heads mark active fan sampling which guarantees a representative sample is taken and therefore enhances measurement accuracy. The values can be displayed in either ppm or mg/m^3.Aeroqual ozone monitors are used by several authors for the

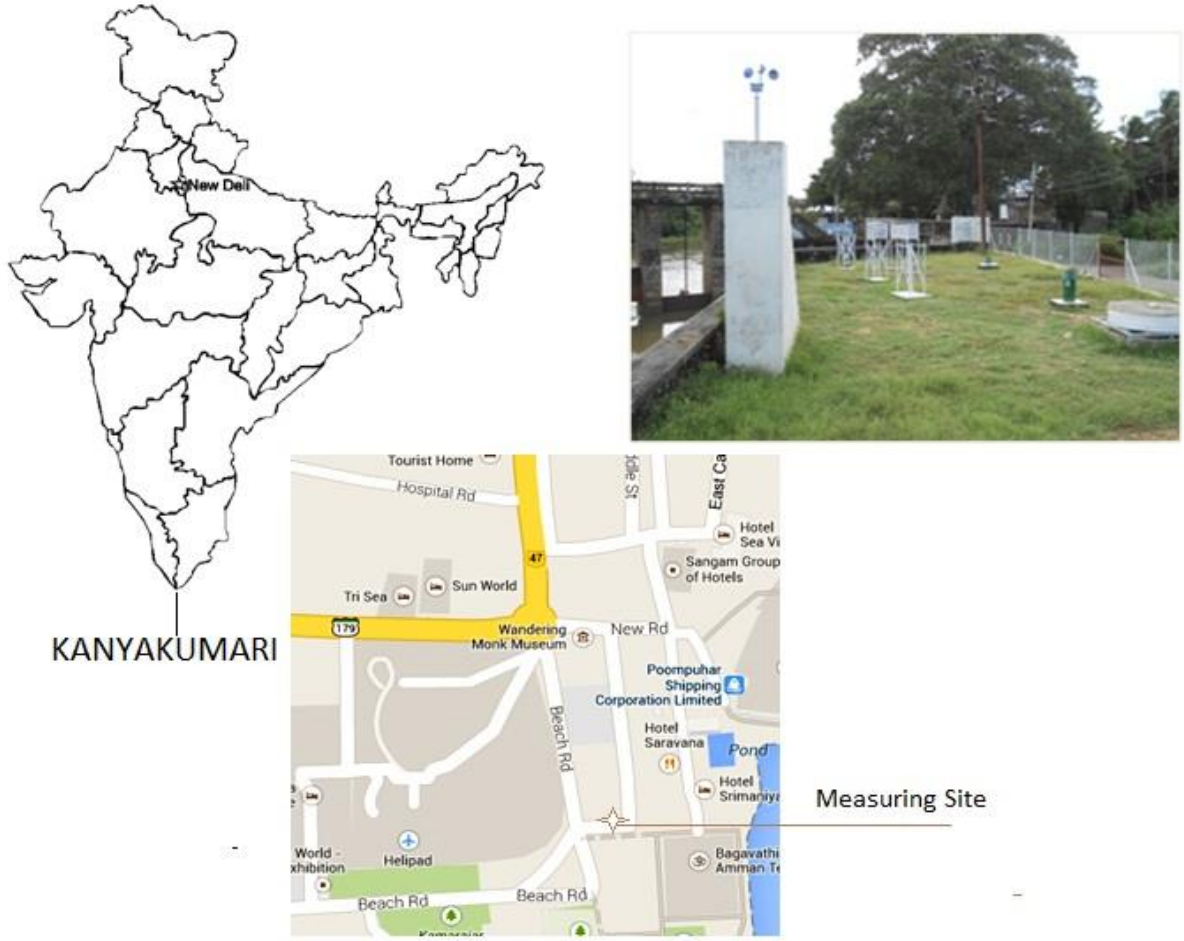

Fig. 1. Kanyakumari (8.0780° N, 77.5410° E; Study area)

measurement of ozone and nitrogen dioxide (Akram, 2008a, 2008b; Su Lee and Shih-Wei Tsai, 2008; Michael Frei *et al*., 2008; DovilėLaurinavičienė, 2009; Chang-fu Wu *et al*., 2010; Jallad and Espada-Jallad, 2010; Cattaneo, 2010).Meteorological observations have been made at the site using weather stations installed on the ground level by Central Water Commision, India. These observations present meteorological parameters such as temperature,pressure, precipitation, and wind speed/direction in 5 min resolution. The meteorological readings were also collected from IMD Website.

RESULTS AND DISCUSSION

Diurinal variation

Cyclic or diurnal stands for the day-to-day variation of Surface O_3concentration. In general, surface O_3follows a clear diurnal cycle. Diurnal variational studies help in understanding the general pattern of variation of a particular species occurring day and night. Generally, a well-marked diurnal variation of Surface O_3concentration occurs in the comparatively unpolluted air during calm weather. The diurnal variation is generally characterized by a broad minimum at night, a quick rise in the morning after sunrise and a sharp maximum near noon (Widen, 1966).In the study area, Surface O_3concentration showed a clear diurnal pattern characterized by lowest values around 0530 Hrs in the early morning, a slow build-up after 0830 Hrs and highest in the afternoon 1430 Hrs Lt. A steady decrease was noticed in late evening hours and the concentration declined further. This forms a clear cycle which shows the association between the build-up of prominent ozone

precursor gases in the morning followed by photochemical ozone formation during daytime. The lower concentration observed in the morning hours is due to the lower boundary layer height that predominantly lowers the mixing process between ozone poor surface layer and ozone rich upper layer. The mixing ratios of ozone increasesslowly after sunrise, attaining maximum values during local noon time (Nishanthand Satheesh Kumar, 2011). Daytime higher ozone levels are mainly due to the photochemical production of ozone (Naja and Lal, 2002). Apart from the role of solar flux, boundary layer meteorology and dynamics also play a key role in ozone variability (White et al., 2002). Boundary layer reaches the maximum height during afternoon hours due to the increase in surface heating. During this time, trace species gets dynamically mixed within, thus forming a convective mixed layer (Reddy et al., 2008). The overall diurnal variation during the summer season throughout the entire period is shown in the Figure 2. From the diurnal variations, it is evident that the ozone concentration tends to be highly related to the amount of sunlight throughout the day. During the early morning hours, when the sun starts to shine, the ozone production rate starts increasing because the sunlight helps in increasing ozone production rate. Moving towards the midday time when the sunlight is strongest, ozone production becomes higher. The increase in ozone concentration during daylight hours is attributed to the photolysis reactions of NO_2 and photo oxidation of VOCs, CO and hydrocarbons. It is also attributed to the downward transport of ozone by the vertical mixing (Tyson et al., 1988).

Summertime variation of Surface O_3

Ozone concentrations also differ seasonally. Ozone concentrations tend to be the maximum during the summer and early fall months. In places characterized by coastal marine layer during summer, the peak ozone season tends to be in the early half of the season. Additionally, as air pollution standards have made some serious controls to reduce the emissions of ozone precursors and the reactivity of VOCs, ozone concentrations have declined faster during times of the year when temperatures and the amount of sunlight are less than during the summer.

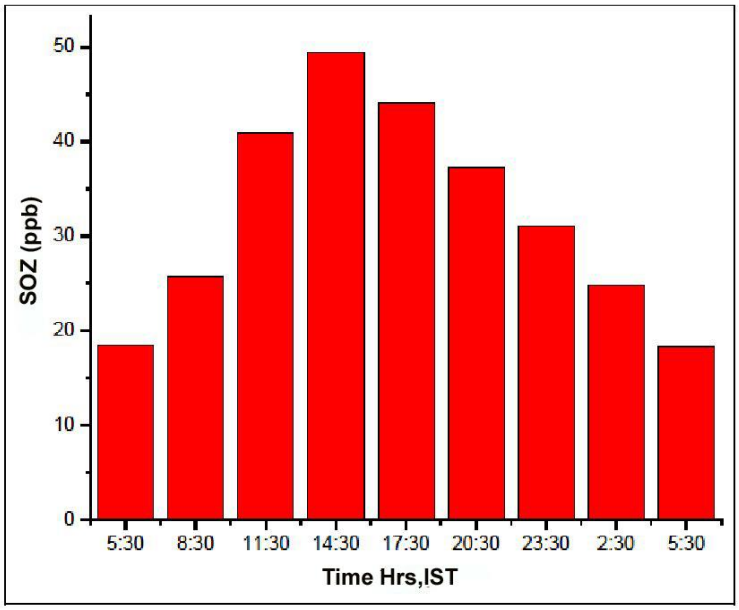

Fig. 2.Diurnal variation

Table1.Surface O_3–Summer Average(SOZ concentration in parts per billion (ppb))

				2010-11					
Month/time	*5.30*	*8.30*	*11.30*	*14.30*	*17.30*	*20.30*	*23.30*	*02.30*	*5.30*
March	17.4	24.29	39.32	48.81	44.6	37.38	29.52	20.53	17.71
April	18.38	24.55	39.84	48.52	43.39	37.69	30.98	22.51	17.57
May	17.5	23.98	36.2	47.91	43.27	34.56	29.62	20.74	17.45
				2011-12					
March	16.7	26.03	40.57	47.35	42.2	34.83	29.04	21.22	18.16
April	16.9	25.06	40.41	49.63	43.57	37.02	31.69	23.2	17.36
May	17.2	25.57	41.37	49.87	46.45	40.38	31.56	22.39	18.71
				2012-13					
March	18.75	26.46	41.3	50.43	42.77	37.09	29.68	22.16	18.79
April	19.38	26.98	43.92	50.82	47.07	39.63	33.33	25.00	19.17
May	18.38	25.11	41.03	48.5	44.5	38.69	32.75	23.8	18.17
				2013-14					
March	19.38	26.57	42.11	50.04	42.77	36.91	31.75	31.54	18.78
April	19.25	27.69	43.76	51.28	44.11	37.98	31.31	32.00	19.87
May	18.13	25.99	41.64	49.17	41.34	36.8	30.23	33.18	18.41

During early morning surface warming by the sun dissipates the radiation inversion and thus permits the mixing of the air from aloft with surface air. Such a process can cause and increase Surface O_3 concentration. Furthermore, the transport of ozone and its precursors downwind from industrial area is also possible. Urban plumes can enter over hundreds of kilometers downward and cover thousands of square kilometers. Table 1 shows the averaged values of Surface O_3 during summer months for four years.

The variation in ozone concentration in different seasons may be due to the variation in NOx, CO, CH_4, hydrocarbon levels and changing meteorological conditions like solar radiation, temperature, cloud coverage, wind velocity, wind direction, relative humidity and rainfall. Many studies show that high values of Surface O_3 occur during the summer season when compared to other seasons. High levels of average O_3 concentrations were reached in summer, followed by the south west monsoon and winter and low values at NEM (Elampari, 2011). From Table 1, it is clear that the summer months of the year 2013-14 recorded high values of Surface O_3 concentration especially during noon hours. The morning 0530 hrs Surface O_3concentration varied between 16 ppb and 21 ppb, and these values are noticed only during the summer months. One more important observation made in this study is the formation of a well pronounced secondary peak in Surface O_3during 0230 hrs particularly in the year 2014. Whenever ozone showed secondary peak in the study area, the wind was strong. A possible explanation of the nighttime ozone peak is the vertical mixing of ozone from the residual layer to the ground, which is caused by a nocturnal low level jet (Corsmeier et al., 1997). In the study area, no evidence for low level jet has been reported. Therefore, the increase in ozone during night time is mainly attributed to the low titration of ozone by oxides of nitrogen (Corsmier et al., 1997) reported that the nocturnal ozone peak was typically in the order of one half or one third of the daytime peak. Figure 3 shows the summer time variation of Surface O_3 during the period of study.

The daily average Surface O_3 value during the summer season of the entire study period is shown in Figure 4. It is evident from the figure that the daily average of Surface O_3 shows an increasing trend in the study area during the summer season. The reason for this is primarily due to the increase in the precursor gas emissions and varying meteorology.

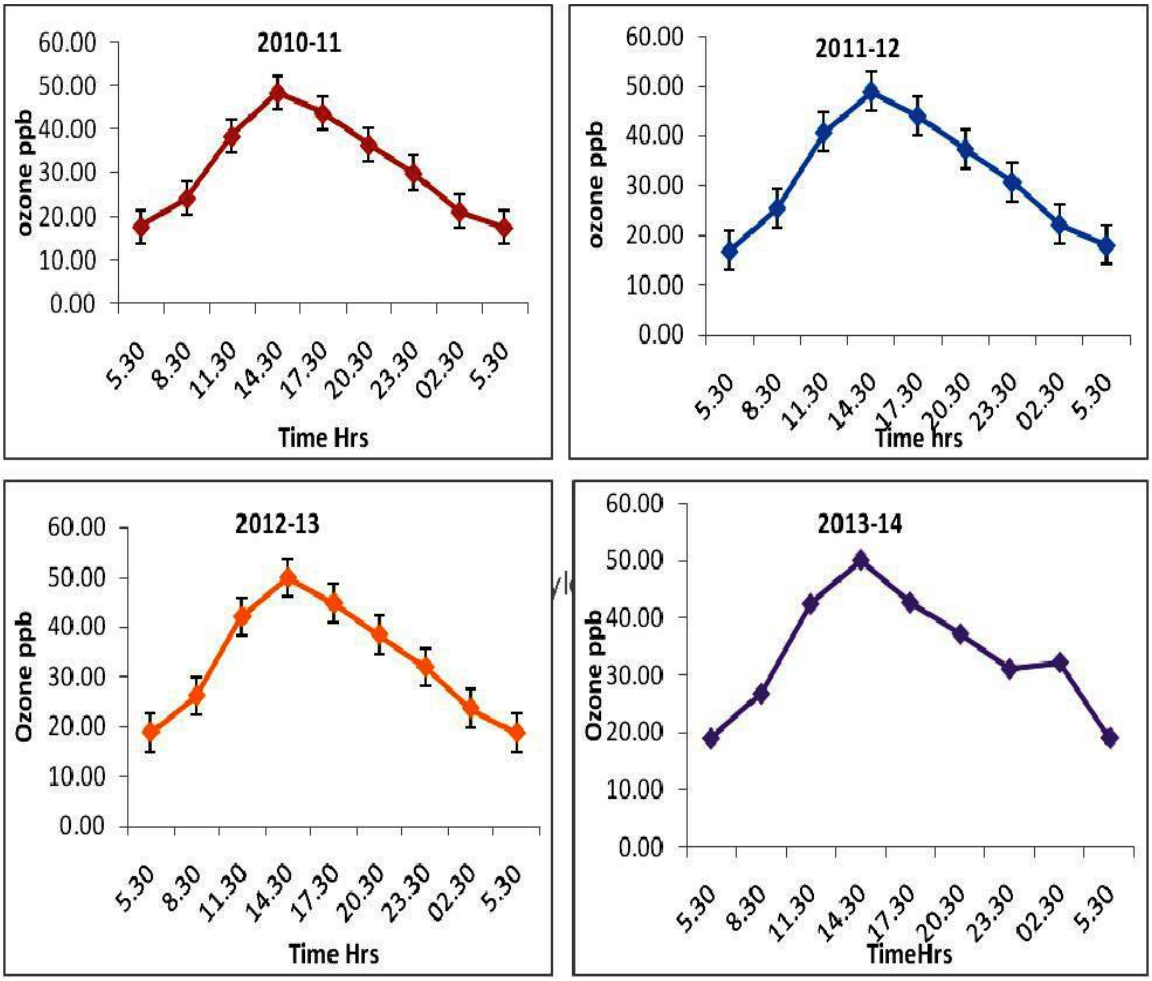

Fig. 3. Summer time Surface O_3

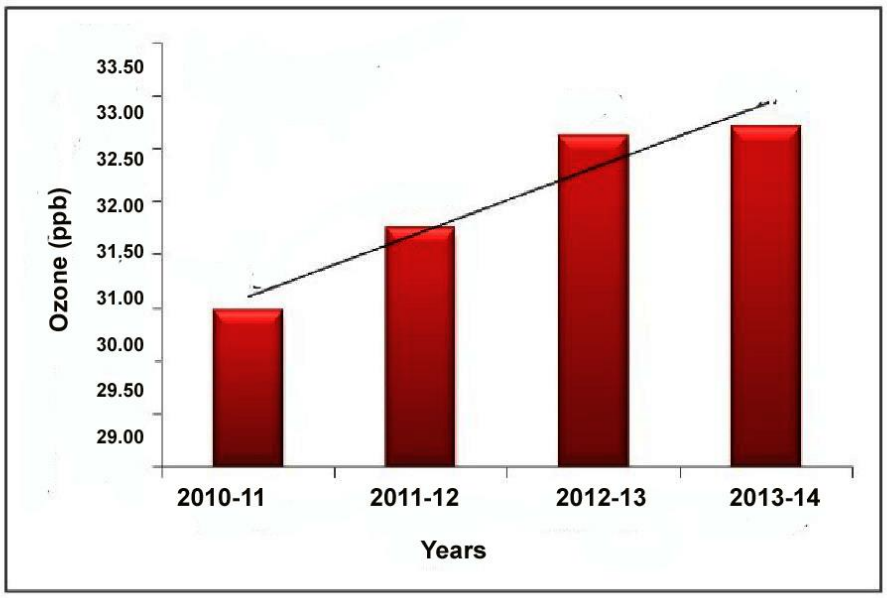

Fig. 4. Daily average of SurfaceO_3 during summer

Ozone weekend effect

A Phenomenon of higher Surface O_3concentration on weekends (Saturday to Sunday) compared to weekdays (Monday to Friday) is referred to as the weekend ozone effect despite the lower emission of anthropogenic precursor gases on weekends (Debaje and Kakade, 2006).Since the 1970s, differences in weekend versus weekday ambient ozone concentrations have been noted in North America. In the early 1970s, studies found higher or comparable ozone and lower nitrogen oxide (NO_x) and volatile organic compound (VOC) concentrations on weekends compared to weekdays in New York City, Washington, DC, and Los Angeles (Cleveland and McRae，1978; Lebron, 1975). Generally, one would expect a high amount of Surface O_3 concentration during weekdays because of increased NO_X production due to high vehicular activity. However, Surface O_3 concentration is higher on weekends than weekdays in spite of low vehicular commuter traffic emission of NOx over the tropics. In the study area, weekend effect was observed during the summer months of 2013-2014 predominantly during April. The weekend effect observed in the diurnal Surface O_3 values is depicted in Figure 5. Different hypotheses have been proposed by several researchers to explain the weekend ozone effect. Apparently, weekend O_3 phenomenon depends largely on differences in NOx concentration between weekdays and weekend, together with the sensitivity of VOC towards the photochemical production of O_3 which occurs quickly for some VOCs at low NOx concentrations (Qin et al., 2004). In the study area, during weekdays, because of predominant vehicular activity, large amounts of oxides of nitrogen were emitted and this in turn destroyed the available Surface O_3 concentration. But during the weekends, the vehicular activities were relatively low leading to the accumulation of Surface O_3 concentration.

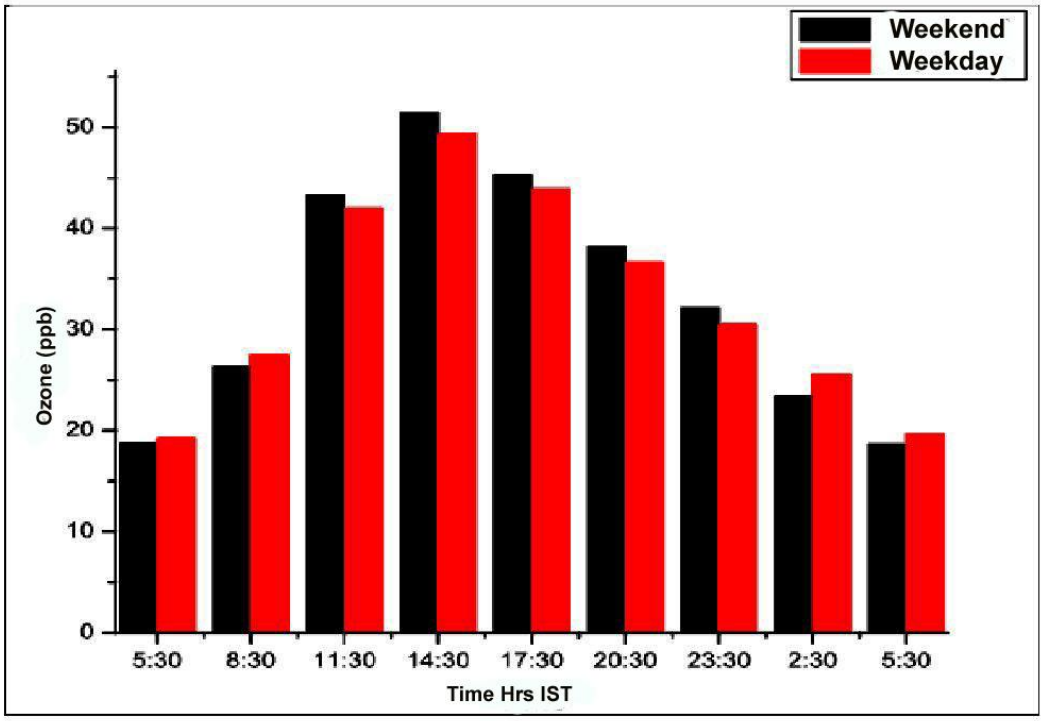

Fig. 5. Ozone weekend effect

Variations of ozone precursors

- **Nitrogen dioxide (NO_2)**

During the summer season the photochemical activity will be more and vehicular emissions will be high. Because of this, the atmosphere can hold large amounts of NO_2 concentration and this will be converted to ozone. In the study area, Surface $O_3$was higher in the summer due to the presence of high levels of NO_2 concentrations during the summer months which were then photolytically converted to Surface O_3. The observed diurnal cycle of NO_2 showed two distinct peaks over a period of 24 hours. The first peak occurred around 0830 Hrs while the second peak occurred at around 2330 Hrs.On analyzing the doublet NO_2 peaks, it was noticed that the highest values occurred during the night. In between these two peaks, a minimum value was observed during the noon time around 1430 Hrswhich is shown in Figure 6. This minimum value suggested the high photochemical conversion rates of NO_2 to Surface O_3concentration in the study area.During 1430 Hrs the atmosphere of the study area recorded maximum Surface O_3 concentration and minimum NO_2 concentration. During the entire period of study, NO_2 concentration varied between 1 ppb to 9 ppb.

The gradual increase in NO_2 concentrations between 0530 Hrs and 0830 Hrs was mainly due to the slow increase in traffic flow. This may be also linked with weakness, which is the characteristic of the nocturnal stable boundary layer, that still persists in the first hours of the morning (Teixeira et al., 2009). The decrease of NO_2 in the late morning hours indicated the build-up Surface O_3 concentration in the atmosphere. The concentration of NO_2 usually declined from its peak as the ozone levels raised and NO_2 concentrations attained its minimum level in the afternoon, at which the production of ozone was maximized. Eventually, after the sunset, the photochemical reaction stops and hence ozone concentration declined while NO_2 concentrations increased in the difficult nighttime chemistry of the atmosphere. Another factor that influences the concentrations of NO_2 is the height of the mixing layer over the observation area. The report obtained from the Regional Transport Office of Nagercoil, TamilNadu, India suggested that the number of vehicles, including trucks, cars and light vehicles registered in the district during the span of five years from 2009 to 2014was found to be increasing and shown in Figure 7. This could be one of the main reasons for rising NO_2 concentrations and in turn Surface O_3 levels. The number of vehicles is increasing year by year and road traffic is the main contributor of NO_2. Diesel vehicles are known to be significant emitters of NO_2 (Kousa et al., 2011).

- **Carbon Monoxide (CO)**

The observed diurnal cycle of CO during the summer months of 2013 and 2014, depicted in Figure 8, shows almost three distinct peaks, two of them during the daytime and one around 0230 Hrs Lt in the early morning. The CO concentration commencedto build up from 0530 Hrs and gradually increased, leading to a maximum value around 0900 Hrs. One of the important sources of air pollution in urban areas, towns and cities of the developing countries is the emissions from motor vehicle exhausts (Mayer, 1999).In the rural areas, CO emission may largelybe due to combustion of fossil fuels and biomass fuels. India, one of the rapidly developing countries of the world, has registered a sharp increase in vehicular pollution, particularly in urban areas(CPCB, 1999). The peaks observed for CO concentration in the study area were because of the gathering of CO near the surface. The diurnal pattern exhibited a narrow, suddenly rising morning peak, followed by a minimum value around afternoon hours and a sudden increase in the late evening hours

and a gradual decline. Once again, there was an increase in the CO concentration around 2330 Hrs. The ambient CO shows high values during the morning hours and close to midnight.

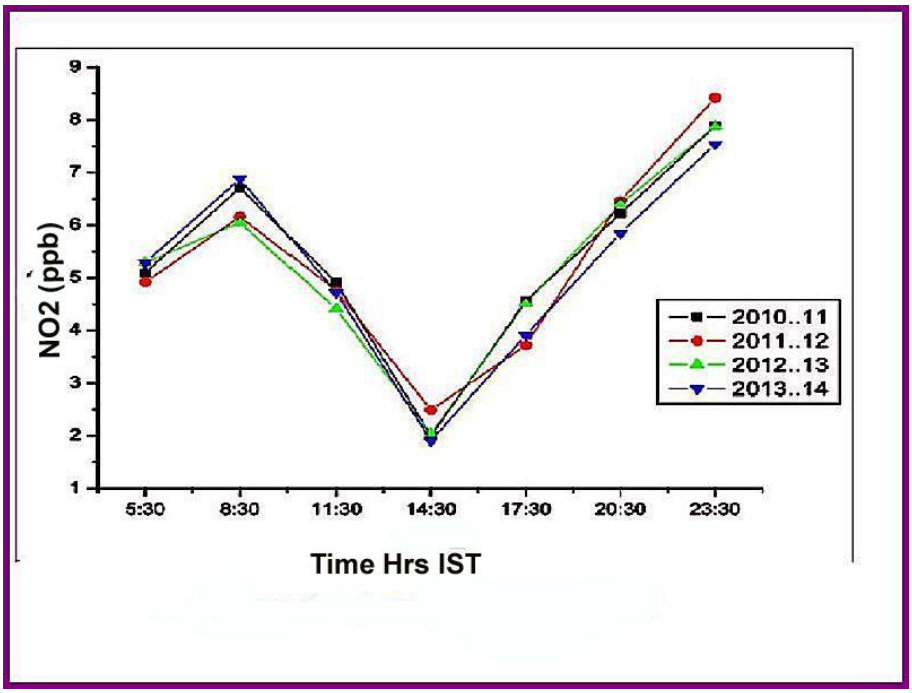

Fig. 6. Diurnal variation of NO_2

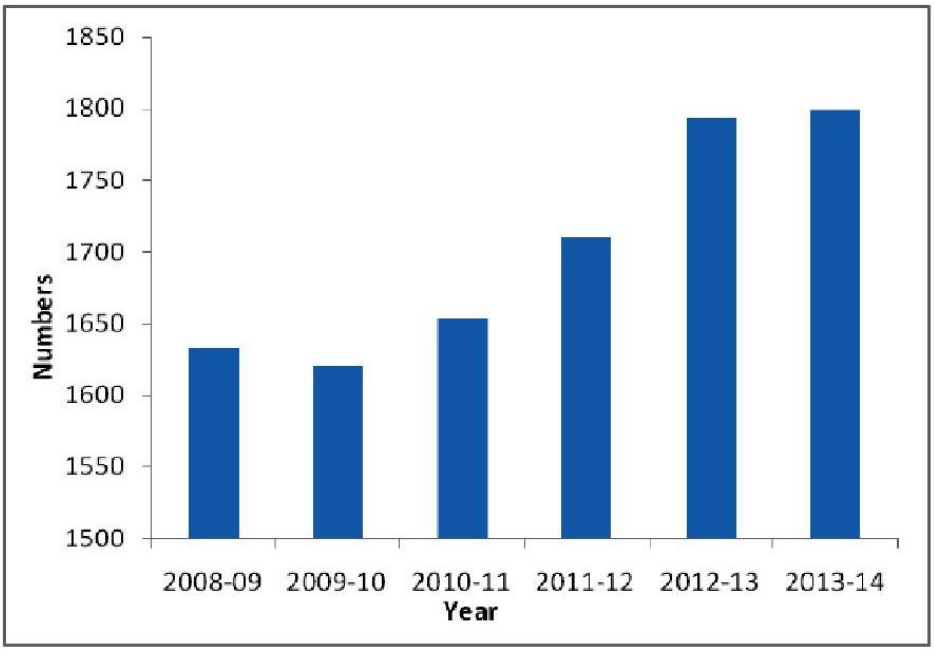

Fig. 7. Number of vehicles registered

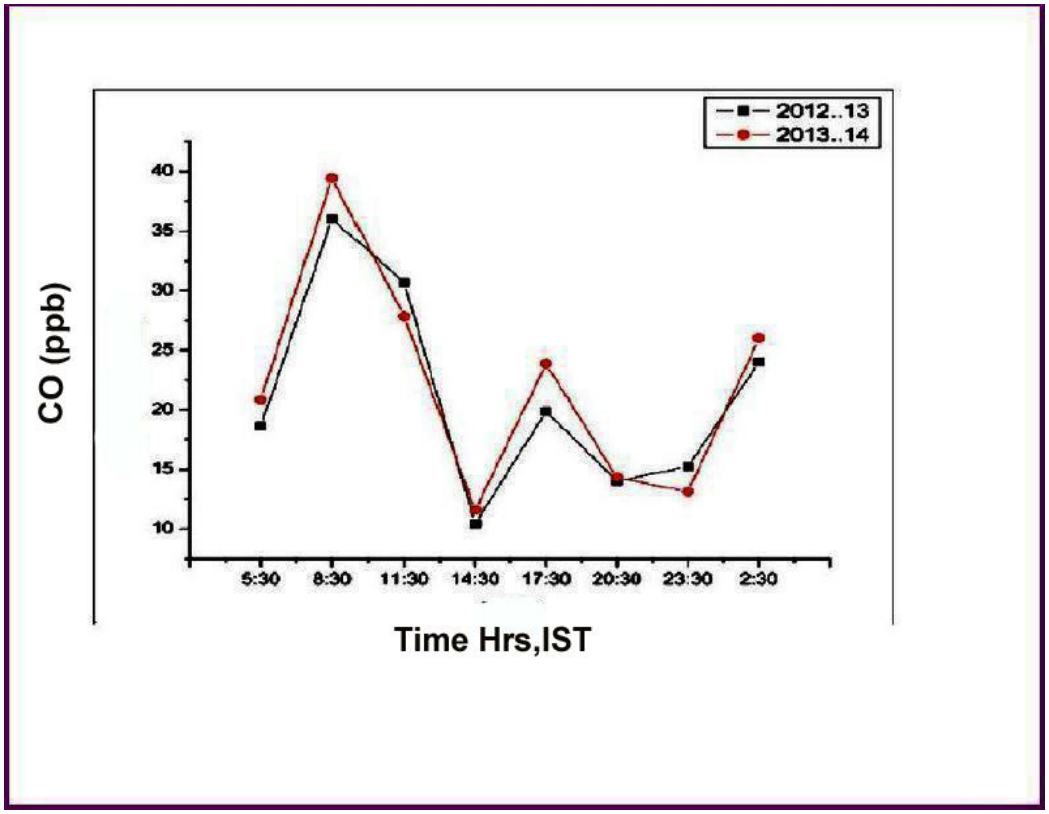

Fig. 8. Summer time diurnal variation of CO

The vehicular emissions will be high during morning hours and this has shown a reflection in the CO concentration. This was the main reason for the sudden accumulation of CO concentration during morning and evening hours. Apart from the vehicular traffic, there are large numbers of hotels in the study area and most of them relie on unprocessed solid fuels for cooking. Current estimates indicate that the combustion of fossil fuels and biomass fuels contributes about 44% of the total global CO budget (Khalil and Rasmussen, 1990), so it is very difficult to say that the CO emission in Kanyakumari is only due to vehicular emissions. During the late afternoon hours, the frequency of the vehicles will be generally low and thereby resulting in low CO values. During night hours, the boundary layer height goes down and stays low till early morning, thereby resisting the mixing of the vehicular emissions with the upper layer. Hence pollutants get trapped in the shallow surface layer and show higher levels (Reddy, 2008). Even though studies show two distinct peaks for CO concentration, the current diurnal pattern can be well compared with the studies of Mohan Kumar et al. (2008) at Jaduguda. The comparison of the diurnal pattern of CO at Kanyakumari with various study areas is depicted in Figure 9.

- **Methane (CH_4)**

Many studies reveal that the diurnal variation of methane is not clear because the concentration not only depends on anthropogenic sources and biomassburning, but also on the soil temperature and the different stages of crop. The diurnal variation of CH_4 is given in Figure 10.

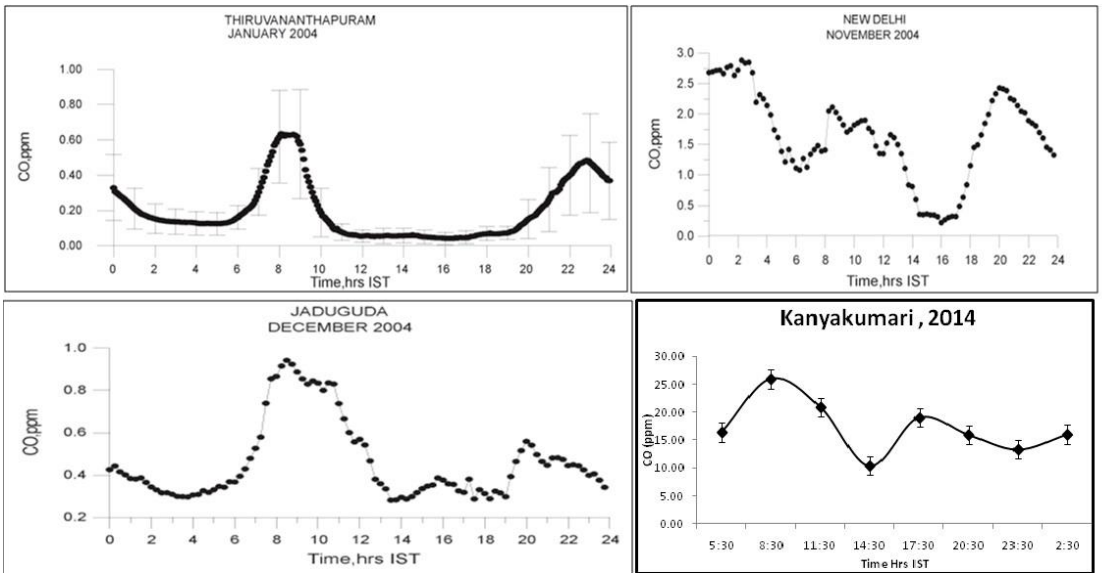

Fig. 9. Diurnal Coincidence of CO with other sites

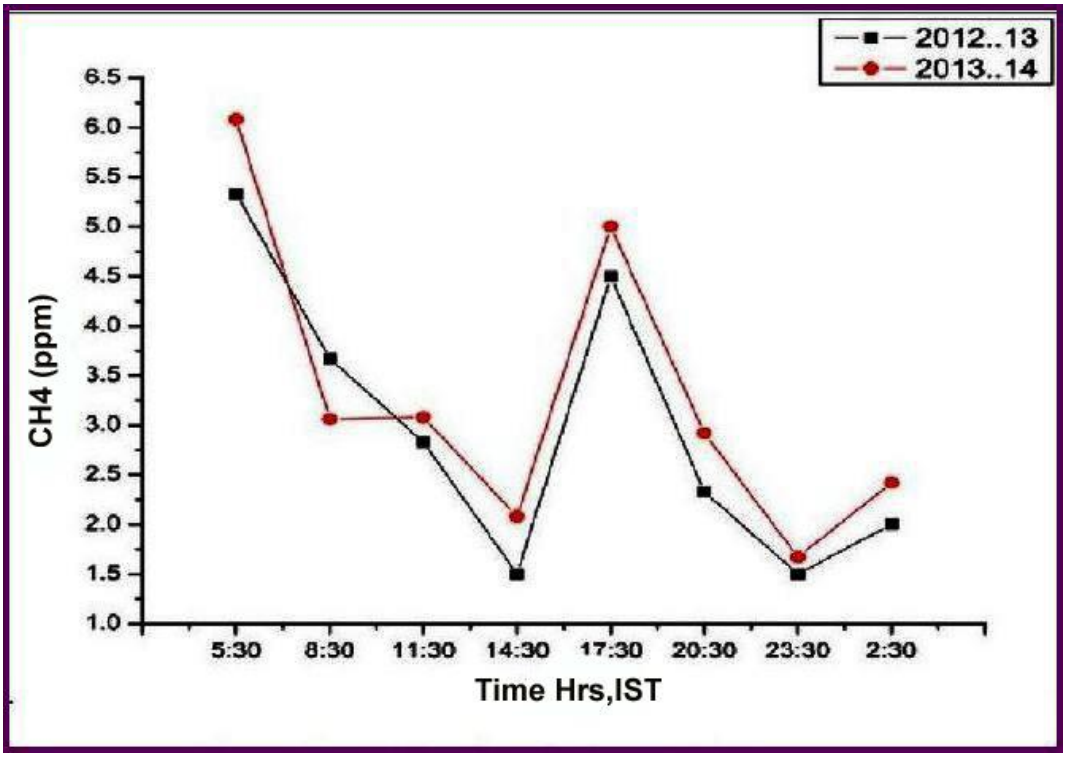

Fig. 10. Diurnal variation of CH_4

There was anoticeable diurnal pattern in methane with two separate peaks one during an early morning time, and one around 1730 Hrs Lt during evening. The sunrise peak was consistent with two way transport mechanism, convective at daytime and diffusive at night-time. Then there was a drop in the methane concentration till 1430 Hrs. The low values occurred during 1430 Hrs and 2330 Hrs. The maximum peak was observed around 1730 Hrs in the evening. Due to the large drop in atmospheric pressure in the late morning in comparison to the night, the

evening peak is higher than the early morning peak (Chandrasekhar and Balaji, 2012).This type of double-peak is often seen in "urban pollutants" such as carbon monoxide, where the morning and evening rush hours lead to elevated mole fractions (Panday and Prinn, 2009).

Association between surface O_3 and precursors

The correlation of Surface O_3 with and the precursors was found and is given in Table 2. Surface ozone exhibits a very complex and non-linear relationship with its precursor NO_x. Higher ozone levels are always associated with air masses impacted by higher NO_x emissions that have been photochemically processed (Olsyna et al., 1994). It is now a well-established fact that NO_x is a principal precursor of ozone photochemical production but there is much uncertainty regarding the factors controlling the ozone yield per unit NO_x (Chandrasekhar and Balaji, 1992).The variation of NOx starts first followed by Surface O_3. The reason for the uncertainty is that the variation of Surface O_3 levels doesn't only depend on the NOx concentration but also on other precursors. Even though oxides of nitrogen act as a dominant precursor of Surface O_3, an X% decrease in NOx levels will not contribute to the X% decrease in Surface O_3. The O_3 and NO_2 profile clearly indicates that the diurnal variation of O_3 and NO_2 is complemented with each other. While the morning and the night low ozone values are associated with high NO_2 values, the afternoon high ozone values are observed with low NO_2 values. In the morning hours, as there is no sunlight till 0530 Hrs, no photochemical process exists and hence the night time chemistry dominates with the destruction process of ozone. This results in the dissociation of O_3 into NO_2, which increases the concentration of residual NO_2. Hence, higher NO_2 values in the early morning hours and consequently lower O_3 values are observed. As the day progresses, O_3 concentration increases steeply from 0830 Hrs and reaches a maximum value around 1430 Hrs. This behaviour can be explained on the basis of photochemical reactions. The afternoon maximum ozone is the result of the photochemical formation of O_3 for the entire day using NO_2 as a precursor gas. From the observations made, it is evident that there is a strong non-linear relationship between Surface O_3 and NO_2 during summer months. This negative correlation suggests the VOC-Sensitive characteristics of the study area as explained by Seinfield and Pandis (2006).The correlation of Surface $O_3$with CO and CH_4 is weak and negative.

Table2. Correlation Coefficient of SurfaceO_3 and precursors in summer

Ozone	Correlation Coefficient	P-value
NO_2	-0.48	P<0.0001
CO	-0.179	P<0.0001
CH_4	-0.117	P<0.0001

Influence of surface meteorology

Meteorological parameters affecting transport, diffusion, transformation and removal processes are functions of both time and space. Transportation of pollutants and their resulting concentrations depend on meteorological factors such as temperature, wind speed, direction, atmospheric stability and the movement of the pressure systems (Pallavi Marrapu, 2012).The meteorological conditions that help the formation of ozone are intense solar radiation, low wind speed, high temperature and a restricted boundary layer depth (Mckendry, 1994).Radiation and temperature drive the chemical reactions producing ozone, while the boundary layer characteristics and the absence of wind are the factors which respectively lead to the build-up of precursors and limit their dispersion. Clear skies, warm temperature, solar radiation and soft winds are believed to have a great influence on surface ozone concentration (Duenas et al., 2002). Any model for ozone is appropriate to evaluate coarse resolution simulations, as it is fitted to catch background airpollution patterns with

stations at a considerable distance from source areas in rural or remote regions (Schaap et al., 2015). The mean temperature of the air at any place depends on many factors, of which, altitude, latitude, proximity to the sea, the temperature of the sea and exposure are the chief (Rao et al., 1972). It is well known that Surface O_3 is highly variable and the trends derived in one location may not represent the whole region .Many factors exist simultaneously at different times or locations and the real system is much complicated. However, several studies suggest that climate impacts and especially temperatures are strong enough to affect the tropospheric ozone distribution (Hsz, 2007).Temperature and long-term urban warming have a serious impact on urban pollution, resulting in higher ozone concentrations, as heat accelerates the chemical reactions in the atmosphere (Walcek and Yuan, 1999). The diurnal variation of temperature, RH and wind speed during summer months for the entire periodare shown in Figure 11. The output of the multiple regression between Surface O_3 and various meteorological factors is given in Table 3.

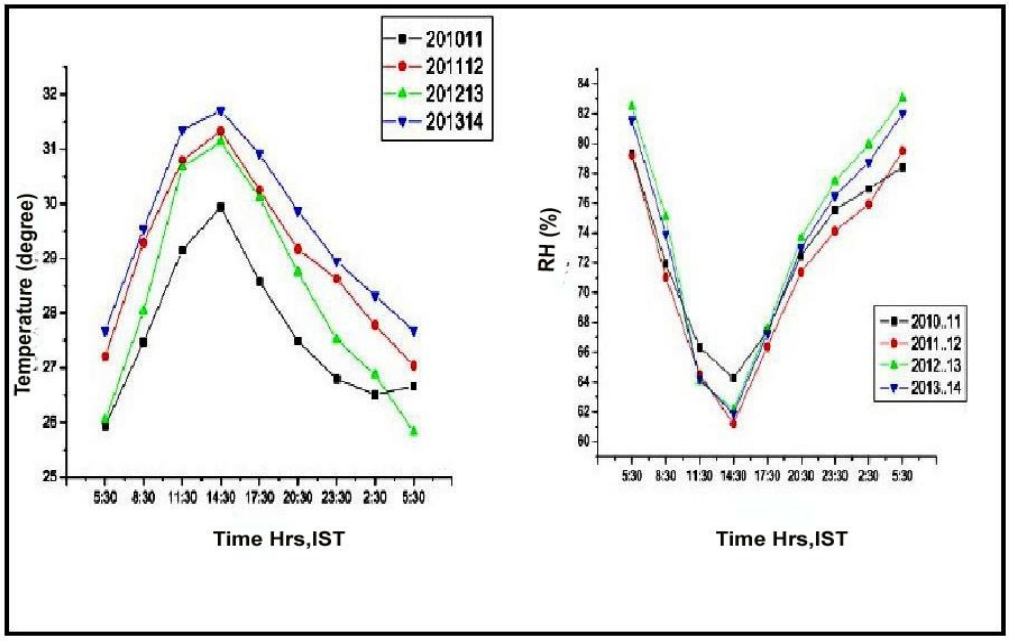

Fig. 11. Diurnal variation of meteorological parameters

Table 3. Multiple regression output table

Primary Factor	Ozone
Variables (Independent)	RH,Temperature,Wind speed
Method	Forward
P-value <	0.05
Coeff.of determination R^2	0.5090
R2 adjusted	0.5085
*Multiple Correlation coefficient R	0.7135
Residual standard deviation	7.174

*The multiple correlation coefficient, R, is the correlation coefficient between dependent and independent variables. Here it is 0.7135, which means, around 71% of the variation of ozone in the study area can be explained with the variation of temperature, wind speed and RH.

The ozone concentration reaches its peak value when the temperature is the maximum which indicates that ozone concentration levels are directly related to temperature. Ambient air temperatures differ with the seasons of the year and time of the day. The overall correlation between temperature and Surface O_3 concentration for the entire study period was found to be positive (r = +0.68, P= 4.314E-05). The positive correlation observed is due to the fact that radiation controls the temperature and hence the photolysis efficiency will be higher during the photon flux. In many ozone monitoring stations there is a positive correlation between hourly wind speed and hourly ozone concentration. The overall correlation between Surface O_3 and wind speed in the study area is positive (r= +0.63, P < 0.0001).Wind and ozone both vary on a similar diurnal pattern with higher wind speeds and higher ozone concentrations usually observed during daytime, and lower wind speeds and lower ozone concentrations usually observed at night. In the study area, the sea-land breezes also play a significant role in the distribution of ozone and transport of ozone from the urban to the coastal and mountain areas. The sea breeze is a weak system, extending vertically to a height of less than 1 km with the wind speed less than 4 m/s. The land breeze can transport the photochemically produced ozone and its precursors over the sea. The accumulated ozone on the sea can return to the land with the sea breeze. This kind of transport tends to contribute significantly to high-ozone episodes in clean coastal and mountain regions (Liu et al., 2002). The overall correlation coefficient between RH and Surface O_3 is negative (r= - 0.54, P < 0.0001).Relative humidity is important because this variable may play a role in the overall reactivity of the system, either by affecting chain termination reactions or in the production of wet aerosols, which in turn affect the ultraviolet actinic flux. Figure 12 shows the variation of wind speed, and Figure 13 depicts the similar variational pattern of Surface O_3 and wind speed. Furthermore, humidity is considered to be astrictive factor in the disposition of NO_2 because high percentages of humidity favor the reaction of NO_2 with particles of NaCl, very common in coastal places (Vera et al., 1997).

CONCLUSION

Continuous measurements of Surface O_3 and its precursors were carried out at Kanyakumari, an attractive coastal spot of South TamilNadu, India. The readings corresponding to the summer months (March-May) were analyzed for the years 2010-14. Surface O_3 followed a clear diurnal pattern throughout the entire period of study. Diurnal variation tends to be highly related to sunlight intensity throughout the day. As a result, during early morning hours, when the sun starts to shine, the ozone production rate starts increasing. Moving towards mid-day time, the sunlight becomes strongest which results in high ozone production. Then the concentration seems to be decreasing in late evening hours. Night time anomaly was observed during the summer months of the year 2013-14, and this can be attributed to the vertical mixing of ozone from the residual layer to the ground. An increasing trend was observed in the daily average of Surface O_3 concentration throughout the study period. This might be due to the increase in the levels of precursor emissions and increased photon flux. A lucid Surface O_3 weekend effect was observed, especially in 2013-2014. This effect is because of predominant NOx-Surface O_3 titrations during weekdays. The precursors of Surface O_3like NO_2, CO and CH_4 showed a clear day-to-day variation. The variation of CO can be well compared with other studies. Surface O_3 showed a negative correlation with all of its measured precursors which confirm the VOC-sensitive nature of the study area.

Surface O_3 showed a strong positive relation with temperature and wind speed and a negative correlation with RH. Measuring more parameters like Cloud cover, rainfall, UV index, precipitation leads to a clear knowledge about the formation and destruction of Surface O_3.

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