

Measurement of surface ozone and its precursor NO_x over urban and rural locations in Kannur- a tropical coastal site in India

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Abstract

Diurnal variations of surface ozone and NO_x (oxides of nitrogen) at Kannur University Campus (12.3N, 75.4E), a rural location and at Kannur Town, an urban location in Kannur (11.9N, 75.3E), a tropical coastal site in the state of India have been studied during winter months of 2009 and 2010. Being an industrially weak area, the study has the uniqueness to reveal the surface ozone production from its prominent precursor NO_x at this site lying along the coastal belt of the Arabian Sea. The maximum value of surface ozone has been observed during day time and minimum during night at two locations. The rate of production and loss of surface ozone is higher at a rural location than an urban location in the same region. This highlights the substantial difference in the ozone chemistry over these two locations.

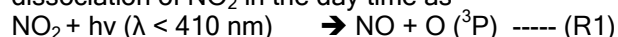
Keywords: Surface Ozone, NO_x, Diurnal Variation, Air pollution

Introduction

The composition of the Earth's atmosphere has been changed by human activity and some of these changes are harmful to human health, crops and ecosystems. The atmosphere contains N₂, O₂ and Ar as major constituents. However there are many other gases which are in low quantities but play an important role in its chemistry and radiation budget. These are divided into two different levels of concentrations, viz minor constituents and trace gases. Ozone is the most important trace gas, which has been talked about ever since it was discovered in the atmosphere (Lal S 2007). Ozone concentration is found to be more in the stratosphere in the height range of 20-28 Km depending on the latitude. In fact, the presence of ozone results in the stratospheric thermal structure by absorbing the harmful solar UV radiation. In the troposphere, ozone is a green house gas which can influence climate and its higher levels even can deleterious effects on the human health and plants (Crutzen 1974). The only mechanism of ozone production is the recombination of atomic oxygen (O³P) with the oxygen molecule. Atomic oxygen (O³P) necessary for ozone production is mainly provided by the photodissociation of NO₂ (λ < 410 nm) in the troposphere where as in the stratosphere it comes from the photodissociation of O₂ (λ < 242 nm) (Chapman 1930; Naja 2004). The production of surface ozone plays a crucial role in the chemistry of the earth's atmosphere, though it is a minor constituent in terms of its abundance (Naja *et al.*, 2004; Subbaraya & Shyam Lal, 1998). Surface ozone does not have direct natural sources, but it is produced in the atmosphere mainly due to its precursors emitted by the increased human activities (Purkait *et al.*, 2009). In the lower troposphere, surface ozone production takes place by photo oxidation of CH₄, CO and NMHCs in the presence of sufficient amount of NO_x (Lal *et al.*, 2000). The most important nitrogen oxides are nitrogen monoxide (NO or nitric oxide) and nitrogen dioxide (NO₂). Main sources of Nitrogen oxide (NO_x) in the atmosphere is due to fossil fuel combustion, fires, microbial soil emissions, lightning, aircraft and

oxidation of biogenic NH₃ (Kleinman 1994). Many studies around the globe have reported that the surface ozone in rural locations near the industrial areas have increased significantly (Khemani *et al.*, 1995; Debaje and Kakade 2006). It has been revealed from the satellite data that the NO_x abundance over Kerala shows an increasing trend over the past few years (Satheesh *et al.*, 2010; Sachin *et al.*, 2009). To retrieve the impact of surface ozone on the radiative forcing of climate, its variation has to be precisely studied using ground based observations. Recently, diurnal and seasonal variations of surface ozone over south Kerala have been successfully classified (Nair *et al.*, 2002) and the results are quite promising to reveal the variation of surface ozone over Kerala. Subsequently, to explore the photochemical production of surface ozone from its prominent precursor NO_x over north Kerala, a study has been initiated in Kannur University to reveal the diurnal variability of surface ozone at two sites in Kannur region which is located along the coastal belt of Arabian Sea.

Surface ozone is mainly produced by the photo dissociation of NO₂ in the day time as



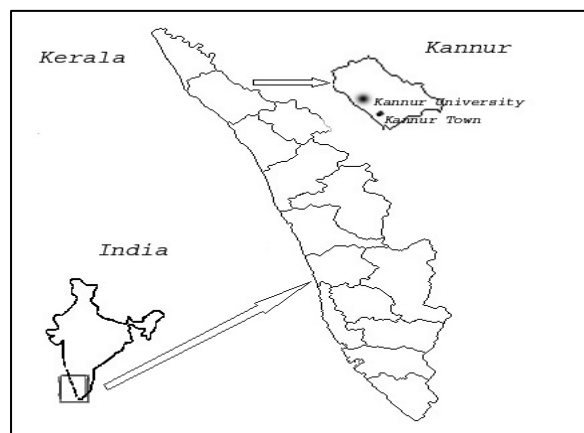
The ozone thus generated can be removed by the titration with NO as



Locations of study and the general meteorology

The two locations selected for observations are shown in Fig.1. Kannur University Campus (KUC) is located in the northern part of Kannur, which is close to Arabian Sea and is situated in an open land. Location at KUC receives plenty of sunshine throughout the day without any shadows. Being this a pristine and unpolluted area, the study would reveal the amount of ozone produced from its various precursors and its chemistry at this location. This analysis will be vital to analyze the radiative processes that have significant impact on the climate changes. Another site is at Kannur Town (KT) which is placed by the side of a national highway where vehicular traffic is very high.

Fig. 1. Locations of two sites of observation



The months December, January and February are characterized by winter at this location and experiences easterly wind during this season. The average weather like relative humidity, solar flux, surface pressure, wind speed, wind direction, rain fall at Kannur during the study period has been collected from a local automatic weather station which is one of the stations of Meteorological and Oceanographic Satellite Data Archival Centre (MOSDAC) established by Indian Space Research Organization at Kannur. The time series variation of solar radiation, surface temperature, relative humidity and wind speed at

Kannur during the period of observations in winter months is exposed in Fig. 2, 3, 4 & 5 and the average weather data is shown in the following Table 1.

Table 1. Average weather data at Kannur during winter

Meteorological parameters	Average data during day time
Relative Humidity	63.52%
Total Solar flux	0.568 KW hr/m ²
Surface pressure	1004.4 mb
Wind speed	3.89 m/s
Wind direction	270 ^o (Easterly winds)
Surface temperature	26.11 ^o C
Rain fall	Nil

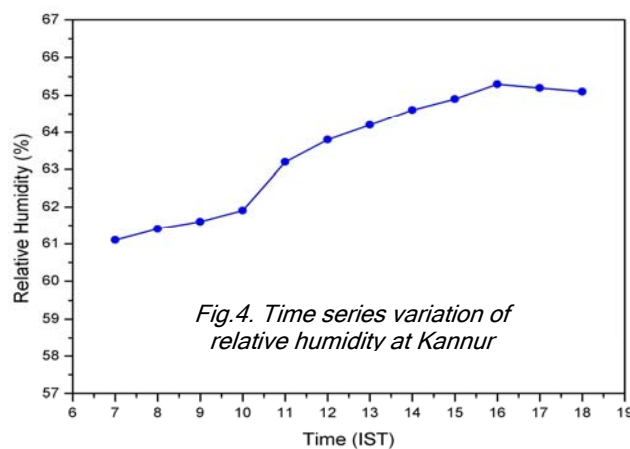


Fig. 4. Time series variation of relative humidity at Kannur

Fig. 2. Time series variation of solar radiation at Kannur

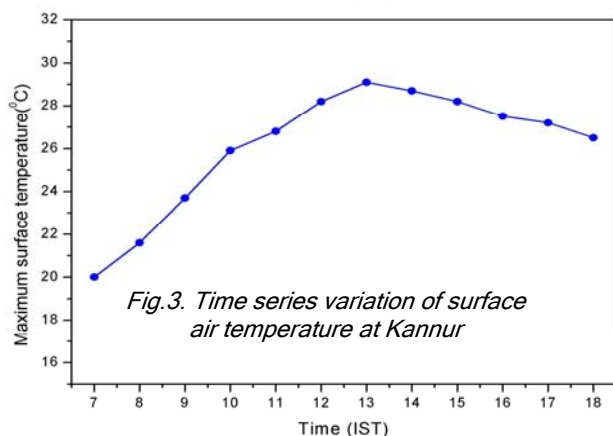
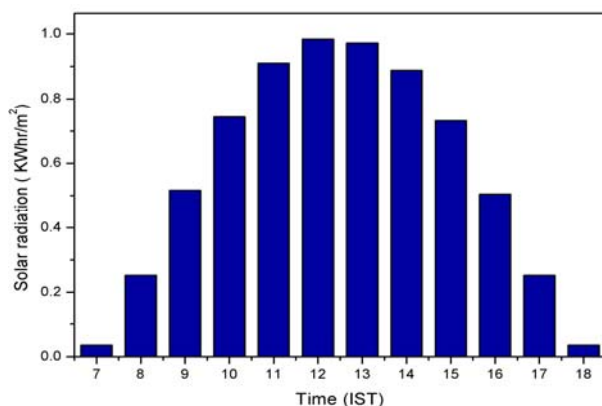


Fig. 3. Time series variation of surface air temperature at Kannur

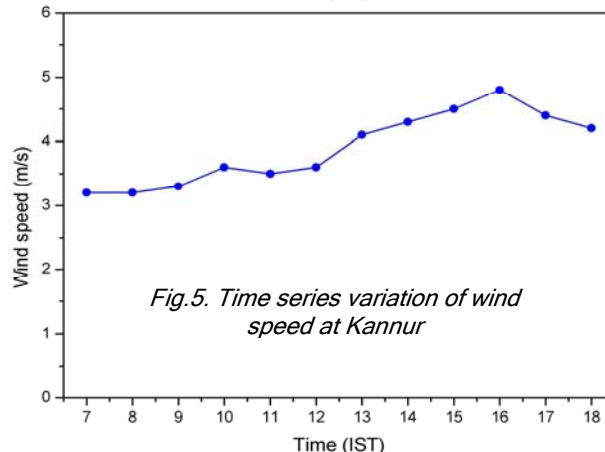


Fig. 5. Time series variation of wind speed at Kannur

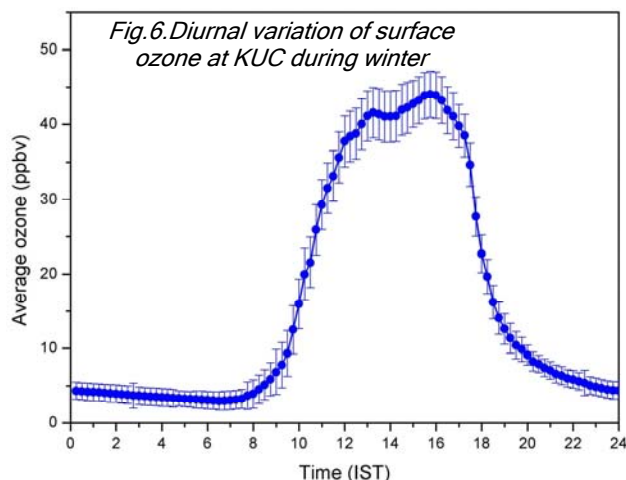
Instruments used for the study

The concentrations of surface ozone and NO_x were measured simultaneously with instruments obtained from Environment S.A., France. The concentrations of ozone was measured using the analyzer (Model O₃ 42M). The principle of measurement is based on the absorption of UV at 253.7nm by ozone present in the sample air. Calibration of the analyzer was performed at regular interval using ozone free air and pure ozone produced using appropriate gas generators. Its low detectable limit is 0.4 ppbv with minimum response time of 20 seconds. The analyzer is provided with an in-built correction facility for temperature and pressure variations as well as the intensity fluctuations of the lamp.

The total NO_x (NO+NO₂) was monitored with standard chemiluminescent analyzer (Model AC 31M) based on the measurement of chemiluminescence (at 630nm) produced by the oxidation reaction of NO of the sample gas with O₃. There is also provision for separating NO and NO₂ components in the NO_x data. The lower detection limit of the detector is 0.35ppbv with minimum response time 20 seconds. The calibration of the system was done using a reference standard NO in cylinders obtained from E.SA Mumbai. These analysers are based on currently accepted technique and are widely being employed all over the globe.

Diurnal variation of O₃ and NO_x at KUC

Diurnal profiles of surface ozone and NO_x observed at KUC during winter is shown in Fig.6 & 7. The vertical lines are one sigma standard deviation. It is observed that surface ozone production at KUC during night time is quite low. The ozone concentration starts to increase during 0800-0900 hr (IST) at all days of observations in winter months. The mixing ratio reaches a maximum during noon time around 1400-1500 hr at which the production of ozone is a maximum resulted from the photolysis of NO₂ as represented by reactions (R1) and (R2). During the late evening hours, around 1800-2000 hr the ozone concentration tends to decrease and reaches to a minimum. Low value of O₃ during night could mostly be due to the absence of photo chemical reaction and its destruction through titration with NO as represented by reaction (R3). This is due to the fresh release of pollutant during the day from vehicular traffic and subsequent photo oxidation of NO₂.



The NO_x (NO + NO₂) concentration reaches its minimum level in the afternoon, at which the production of ozone is maximum. From the figures 6 and 7 a clear anti correlation is observed for the abundances of ozone and NO_x over the KUC during winter months. The average value of day time ozone is 26.92ppbv and maximum value at 1500 hr is 45ppbv and that of night time is 3.62ppbv. The mean value of day time NO_x is 1.65ppbv and that of night time is 2.73ppbv. During 0800-1100 hr,

the rate of change of ozone is 10ppbv/ hr, whereas in the evening, 1700-1900 hr, the rate of change of ozone is - 17.7ppbv/hr.

Diurnal variation O₃ and NO_x at KT

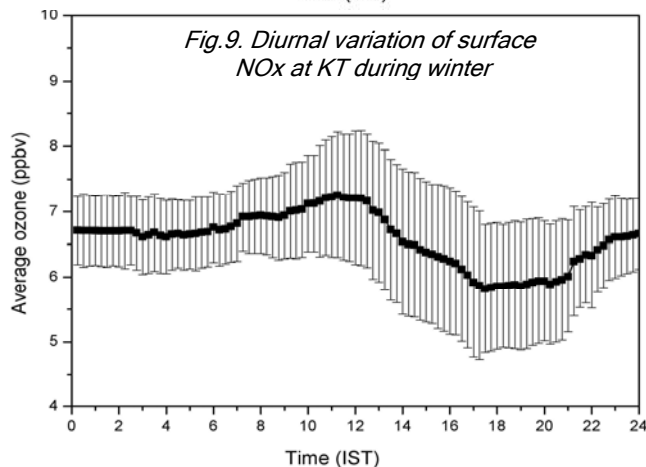
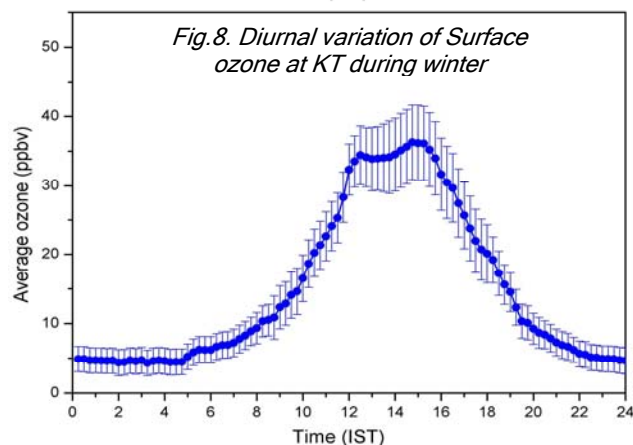
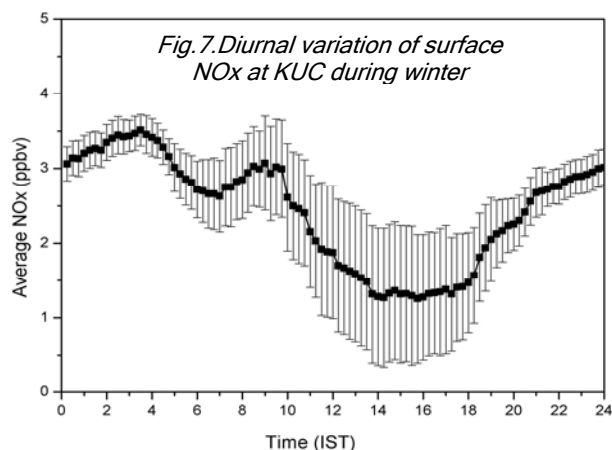
Diurnal profiles of surface ozone and NO_x during winter season at KT is shown in the figures 8 and 9. It is observed a similar profile of ozone and NO_x variations at KUC as well; however, there is a significant change in the production and loss rates of ozone and NO_x. The concentration of ozone during this period is found to be increased from a minimum value of 9ppbv around 0830 hr, to a maximum value of 36ppbv around 1200-1300 hr. In the evening, around 1800-2000 hr, the ozone concentration tends to reach its lowest value of 5ppbv. Higher levels of NO_x during day time are mainly due to extensive vehicular exhaust at this location. The average value of day time ozone at this site is 24.21ppbv with maximum of 35ppbv at 1400hr and during night time is 5.23ppbv. The average value of day time NO_x is found to be 6.81ppbv and that of night time is 5.41ppbv. During 0800-1100 hr, the rate of increase of ozone is 4.6ppbv/hr, whereas during in the evening, 1700-1900 hr, the rate of change of ozone is 5.7ppbv/hr. Table 2 shows the rate of change of ozone and NO_x at these two locations.

Table.2. Observed rate of change of ozone at two sites

Locations	0800-1100hrs (ppbv/hr)	1700-1900hrs (ppbv/hr)
KUC	10.0	-17.7
KT	4.6	-5.7

Discussion

The diurnal variations of surface ozone and NO_x at KUC and KT have been observed and it is found a significant difference in the ozone production and its loss rates at these two locations. This reveals that ozone production and lapse rates are much higher at KUC than that at KT. It is further observed a small decline in the ozone concentration during noon time at these two locations and it may be due to the hectic convective activity on the ground at noon time which can reduce the ozone mixing ratio till it gets stabilized. At KUC, the production and destruction of ozone are quite sharp, while at KT, the period over which maximum ozone concentration existing is less compared to that in KUC. This is due to the abundance of other prominent pollutants present over KT by which they severely affect the mixing of ozone with the ambient air. The observed profile of ozone variation over KUC is quite similar to that have been reported earlier in the case of a rural environment in India where the production of ozone is higher than urban locations (Londhe *et al.*, 2008). This observation could be further substantiate only by accounting the role of other prominent ozone precursors like CO, CH₄ and VOCs present over these two locations. In this connection, attempts are being imitated to explore the significant role of these trace gases on the production and loss of surface ozone at these two locations.



Conclusions

This study is the first attempt in this region which is lying along the coastal belt of the Arabian Sea to explore the production of surface ozone from its prominent precursor NO_x during winter months. The variability of surface ozone and its precursor NO_x have been monitored at KUC and KT during winter months of 2009 and 2010. These two sites are separated by 20 Km, yet the variations of surface ozone and NO_x at the two sites differ significantly. The day time ozone production at KUC is found much higher than that at KT during the period of observation. It is revealed that the ozone production and

loss rates at KUC are much higher than at KT. This may be due to the enhanced loss rate of ozone in rich NO_x environment. The rapid production and loss rates of ozone observed at KUC are mainly due to the less amount of pollution. Relatively low production and loss rate of ozone at KT gives a clear indication that KT is a polluted site, where other prominent precursors play a major role in the chemistry of ozone.

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