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Diurnal variation of Surface Ozone with Meteorological parameters at Kannur, India

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ABSTRACT

Diurnal variations of surface ozone and NOx (oxides of nitrogen) at Kannur University campus (12.26N, 75.39E), a rural location and at Kannur Town, an urban location in Kannur (11.86N, 75.35E), a tropical coastal site in India have been studied during winter months in 2009 and 2010. The study revealed that surface ozone abundance is high at Kannur University campus than at Kannur Town. The maximum mixing ratios of surface ozone during winter at rural and urban sites were found to be (44.01±3.1) ppbv and (36.3±5.4) ppbv respectively, which is a clear indication of the air quality over these two locations during the season. Likewise, the ozone production is higher in the afternoon in winter months which in turn reveal the finger print of photolysis of NO_2^* over these locations. The NOx mixing ratio shows a strong diurnal variability which substantiates the production of ozone from NOx.*

Key words: Surface ozone, precursors, meteorological parameters, air quality.

INTRODUCTION

Atmospheric ozone plays a significant role in maintaining ecosystems on the earth's surface. Tropospheric ozone has a strong absorption at 9.6 μm in the outgoing long wave from the Earth by which it acts as a powerful green house gas. At the surface level it is a major air pollutant and one of the main oxidants [1, 2]. Tropospheric 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 in Indian sub-continent [3, 4]. Photochemical ozone production takes place by oxidation of CH_4, CO and NMHCs in the presence of sufficient amount of NOx and sunlight [5, 6]. Meteorological parameters like wind speed, wind direction, temperature and relative humidity have a massive influence on O_3 concentrations [7]. Increased O_3 concentration is related to the increase in fossil fuel consumption in the automobile, power generation and industrial sectors all over the world to meet the increasing energy demand of the growing population [8]. Tropospheric ozone plays a central role in the oxidative chemistry of the troposphere; it has an important impact on the radiative balance of the atmosphere, and is known to have harmful

effects on human health and agricultural crop production [9, 10]. It has been observed a decrease in the wheat crop yield in China due to an increase in O_3 (above 60 ppbv) at the ground level [11]. The tropical troposphere rich in water vapour and intense solar radiation flux which make this region as the most favorable section for the production as well as transport of many atmospheric gases [12]. Many studies around the globe have reported that the surface ozone in rural locations near the industrial areas have increased significantly [9]. Thus the production and destruction of surface ozone mainly depend on the abundance and chemistry of its precursors. Surface ozone is removed either by dry deposition or by photochemical loss process. It has been revealed that enhanced surface ozone abundance is found in rural areas than in the urban areas. Two mechanisms have been proposed to account for higher surface ozone concentration. One is the transport of its precursors NOx and NHMC [13], followed by in situ photochemical ozone production. Thus a long term investigation is required for classifying the significant features in the atmosphere that can vary the abundance of ozone in the troposphere.

This paper pertains to the investigation of the variations of surface ozone and its prominent precursor NOx at two sites in Kannur, a location along the coastal belt of the Arabian Sea to explore the air quality over this region. The study mainly focuses on the photochemical production of surface ozone from NOx, at two locations; at Kannur University Campus (KUC) a rural site and at Kannur Town (KT), an urban location and has been carried out with the aid of ground based portable gas analyzers.

Surface ozone is mainly produced by the photo dissociation of NO_2 in the day time as:

$NO_2 + h\nu\ (\lambda < 410\ nm) \rightarrow NO + O\ (^3P)$ (R1)
$O\ (^3P) + O_2 + M \rightarrow O_3 + M$ (R2)

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

$O_3 + NO \rightarrow NO_2 + O_2$ (R3)

Where the photolysis rate of NO_2 is J_1 and the rate of reaction (3) is k. In one dimensional steady state condition, ozone concentration is given by:

$$[O_3] = J_1 [NO_2] / (k [NO]) \quad (1)$$

It is very well established that the photodissociation rate depends on $F(\lambda)$ which is the solar actinic flux, $\sigma(\lambda)$ is absorption cross-section of NO_2, and its quantum yield $\varphi(\lambda)$. Thus the total photodissociation rate is the integration over individual J values ranging from 290 nm to 420 nm present in the solar flux and it is represented as:

$$J_1 = \int F(\lambda)\ \sigma(\lambda)\ \varphi(\lambda) \quad (2)$$

MONITORING SITES AND METEOROLOGICAL BACK GROUND

The two locations of observations are shown in Fig.1. Kannur University campus (KUC) is located in the northern part of Kannur district in Kerala state which is lying along the coastal belt of the Arabian Sea and is near to the Western Ghats. The air distance to the sea shore is 4 km and that to the Western Ghats is 50 km. The land area of Kannur is about 3000 km^2 with an average population density of 1000 per square kilometers. KUC is situated in an open land to receive plenty of sunshine throughout the day without any shadows and the land is surrounded by good

amount of vegetation.KUC is situated in an open land to receive plenty of sunshine throughout the day without any shadows. Being a pristine and unpolluted area (12.26N, 75.39E), the study can reveal the amount of ozone produced from its various precursors at this location. Kannur Town (KT) is another site (11.86N, 75.35E) located in the city which is by the side of a national highway where the vehicular traffic is very high.

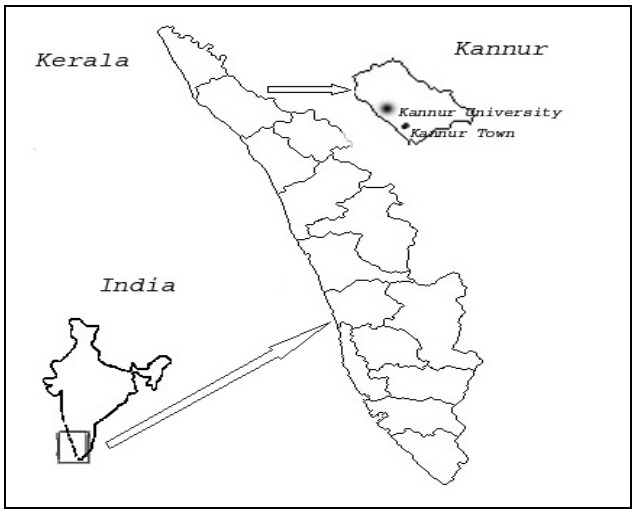

Figure1. Locations of two sites of observation

The most prominent meteorological feature at these two locations is the monsoon rainfall. The south-west monsoon, which usually set in by the first week of June lasts till September. This is followed by the return monsoon or north-east monsoon which lasts till November. On the average, about 90% of the total rainfall occurs from June to November, which constitute the monsoon season. The months December, January and February with insignificant rain and low RH represent winter season, while the months March, April and May are characterized by summer in which high convective activities are observed due to high temperature. The Average weather like relative humidity, solar flux, surface pressure, wind speed, wind direction, rainfall during observation period is shown in Table1.

Table: 1 Average weather data at Kannur during winter

Meteorological Parameters	Locations	
	Kannur University	Kannur Town
Relative Humidity	63.5%	64.2%
Surface pressure	1004.4 mb	1004.3 mb
Wind speed	3.89 m/s	3.92 m/s
Wind direction	270^0	270^0
Surface temperature	26.1^0C	28.2^0C
Rain fall	Nil	Nil

INSTRUMENTS USED FOR THE STUDY

The concentrations of surface ozone and NOx were measured simultaneously with instruments obtained from Environment S.A., France. The concentrations of ozone was measured using the analyzer (Model O_3 42M). The principle of measurement is based on the absorption of UV at 253.7 nm 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 NOx analyzer (AC31M; Environment S.A. France) is based on the chemiluminescence effect produced by the oxidation of NO by O_3 molecules. In the present study, NO_2 is measured by converting it into NO using the thermal conversion (heated molybdenum) method. The molybdenum converter is found to have higher sensitivity and & 100% conversion efficiency (Winer et al., 1974). But it has been realized that molybdenum converter also converts other species such as PAN, HNO_3, other organic nitrates and nitrites into NO (Winer et al., 1974, Naja et al., 2002). However, PAN is thermally unstable at temperatures above 30-35^{0}C, and its concentration may be very small at the surface levels. Thus, the actual concentrations of NO2 and therefore NOx may be lower. However, it has been shown that NOx remains the major fraction of NOy (NOx + products of NOx oxidation) in rural environments. Thus, the NOx measurements presented here should be considered as upper limits to their true values, and so they are represented here as NOx*

There is also provision for separating NO and NO_2 components in the NOx 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.

RESULTS AND DISCUSSION

DIURNAL VARIATION OF OZONE AT KUC AND KT

Diurnal profiles of surface ozone have been retrieved at KUC and KT during winter months of 2009 and 2010 and the average values are shown in figure 2. It is observed that surface ozone production at KUC during night time is quite low. The ozone concentration begins to increase after sunrise around 08:00-09:00h (IST), and attains its maximum level in the afternoon around 14:00-15:00h mainly due to the photolysis of NO_2 as represented by (R1) and (R2). During the late evening hours, around 18:00-20:00h the surface ozone concentration tends to decrease and reaches to a minimum. Low value of O_3 during night could mostly be due to the absence of photodissociation and its destruction through titration with NO as represented by (R3) and surface deposition. At KUC, the concentration of ozone increased from minimum value of 2.9 ppbv at around 08:00h, to a value of 44 ppbv at 15:00h in day time. The low concentrations of ozone observed during morning hours is due to the lower boundary layer height which mainly reduces the mixing process between ozone poor surface layer and the ozone rich upper layer. Boundary layer processes and meteorological parameters also play a significant role in the ozone variabilities.

Mixing ratios of ozone start increasing gradually after sunrise, attaining maximum values during local noon time. After sun rise, boundary layer height gradually increases from about 300-400 m to about 1.5 to 2 km during noon time hours due to convective heating and the layer becomes stratified. During this period, air at lower levels, which has low amounts of ozone, mixes with the air from greater heights which is relatively rich in ozone. Hence average mixing ratio during 13:00h – 15:00h could be representative of upper boundary layer and the free lower tropospheric ozone levels. The photochemical production of surface ozone is a direct consequence of the ambient temperature and the solar flux and its concentration increases with respect to both parameters. From the study the rate of production and loss of ozone at these two locations during the period of observations are tabulated in Table 2.

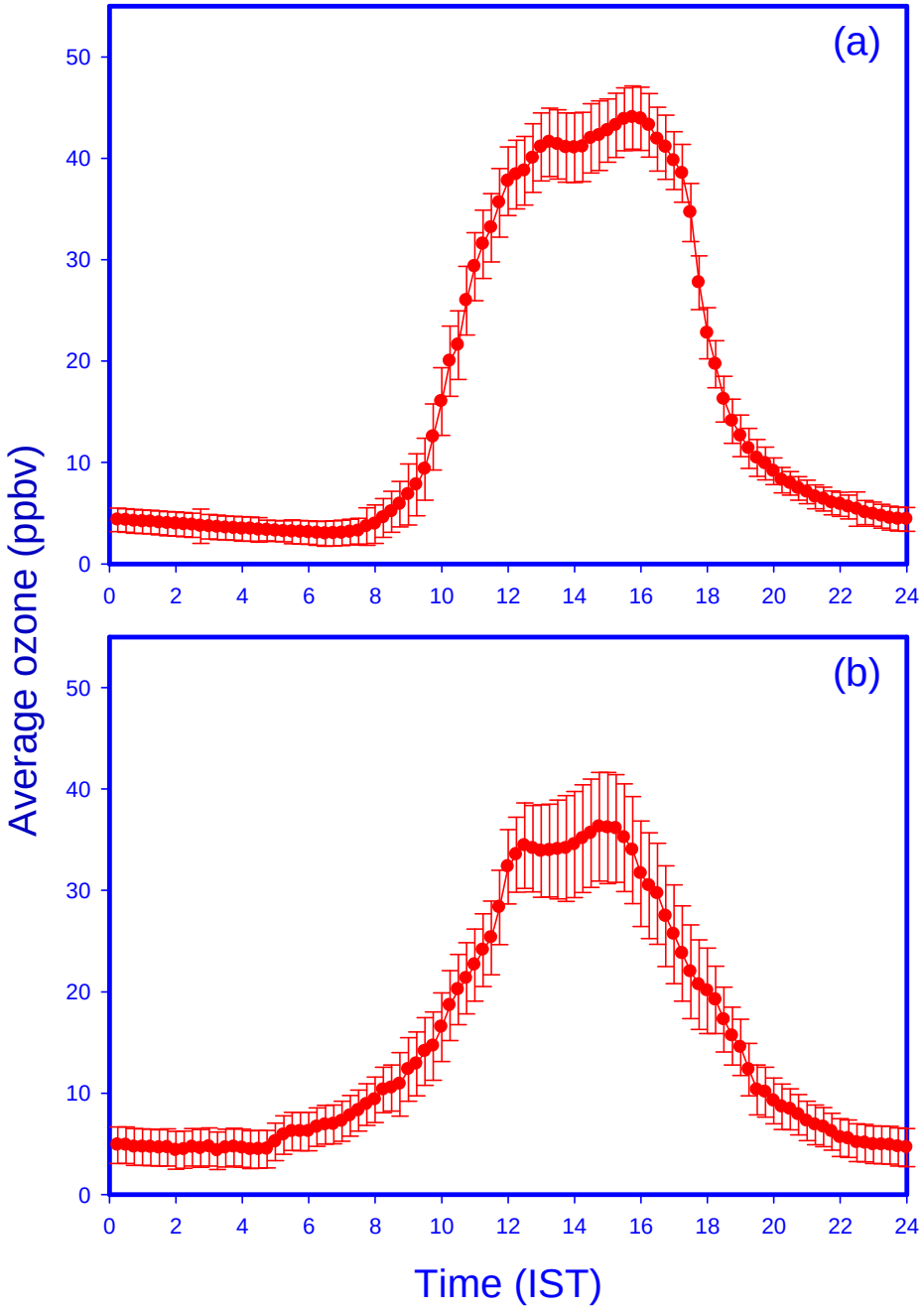

Fig.2. Diurnal variations of Surface ozone at (a) KUC (b) KT in winter months, vertical bars are one sigma standard deviations

Table: 2 Maximum, minimum ozone, seasonal average ozone and the rate of range of ozone at two sites in Kannur

Location	Maximum ozone (ppbv)	Minimum ozone (ppbv	Average ozone (ppbv)		Rate of change of ozone (ppbv/h)	
			08:00-20:00h	20:00-08:00h	0800-1100h	1700-1900h
KUC	44.0	2.9	29.2±4.4	4.4 ±1.9	10.0	-17.7
KT	36.28	4.4	24.1± 3.9	5.7± 2.1	4.6	-5.7

From this, it is clear that the day time O_3 concentration shows maximum (29.2 ±4.4) ppbv at KUC compared to KT (24.1± 3.9) ppbv, due to the heavy pollution present at KT. KT being an urban

location, other prominent precursors like VOC, NMHC, CO, may play a crucial role in the chemistry of ozone. Maximum and minimum ozone concentrations observed at KUC and KT were 44.0ppbv and 36.28ppbv respectively. It is further noticed that the rate of production of surface ozone and its loss during winter months are found to be maximum (10.0ppbv, -17.7 ppbv) at KUC, a rural location whereas they are minimum at KT (4.6 ppbv, -5.7ppbv) an urban location in Kannur district. This can be attributed to the shrink in boundary layer height, as well as relatively high precursor gas concentration at the surface layer. The net loss of ozone observed rather late in the evening is due to slow titration of ozone because of low NOx concentration. Further, a considerable amount of vehicular emission at KT turns it to become a rich NOx environment at which the titration process of ozone would dominate more than its production.

DIURNAL VARIATION OF NOX* AT KUC AND KT

Fig.3 represents the diurnal profiles of NOx* at these two locations during the same period. It is observed that NOx* mixing ratios are generally stronger during morning and late evening hours.

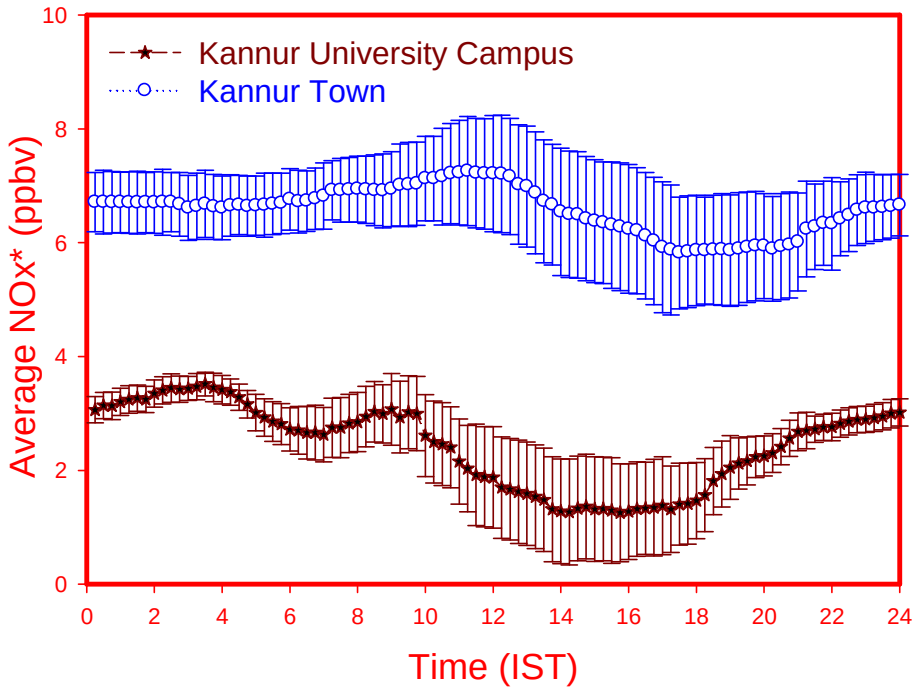

Fig.3.Diurnal variation of surface NOx* at KUC and KT during winter months

Table 3: Maximum, minimum, day time and night time average NOx* observed at KUC and KT

Location	Maximum NOx* (ppbv)	Minimum NOx* (ppbv)	Average NOx* (ppbv)	
			08:00-20:00h	20:00-08:00h
KUC	3.5	7.3	1.9	2.9
KT	1.3	5.8	6.4	6.6

The shift in the diurnal variation of NOx* at these locations is due to the variation in the emissions and transport of NOx* in the urban and rural locations. Variations in NOx* are caused by change in boundary layer mixing processes, chemistry, anthropogenic emissions and meteorological parameters [14, 15]. The emitted pollutants get trapped at the lower heights in the boundary layer during evening and continue to remain till early morning due to the formation of a nocturnal stable layer. The pollutants are diluted during mid day thanks to the increased height

of boundary layer and extensive mixing thus produced. Average, maximum and minimum values of NOx* observed at KUC and KT is shown in the Table3.

At KUC, the average values of NOx* concentration during day time (08:00-20:00h) and night time (20:00-08:00h) were found to be 1.9 ppbv and 2.9 ppbv respectively and at KT, the average values were 6.4 ppbv and 6.6 ppbv respectively. The maximum and minimum NOx* concentration at KUC were 3.5 ppbv, 1.3 ppbv and that at KT were 7.3 ppbv and 5.8 ppbv respectively during the period of observations. This shows the degree of pollution in KT due to the heavy traffic.

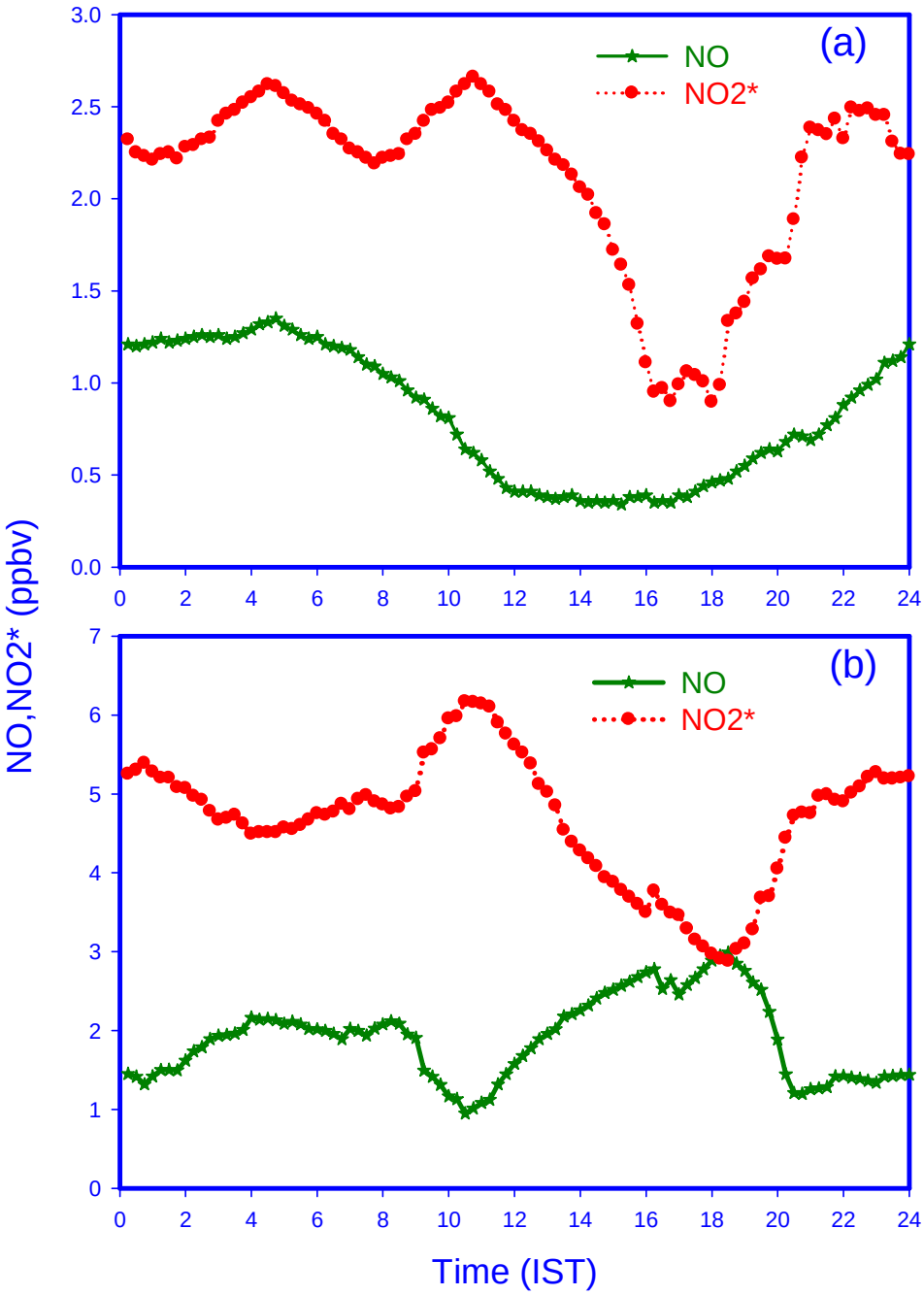

Fig.4.Diurnal variation of NO, NO_2* at KUC and KT during winter months

DIURNAL VARIATION OF NO, NO_2* AT KUC AND KT

Seasonal average diurnal variation of NO, NO_2^* at KUC and KT are shown in the figure 4. From the figure, it is found that the concentrations of NO_2* at KT is relatively higher than that at KUC. The shapes of the profiles at these two locations remain the same, but NO_2* concentration at KT is higher.

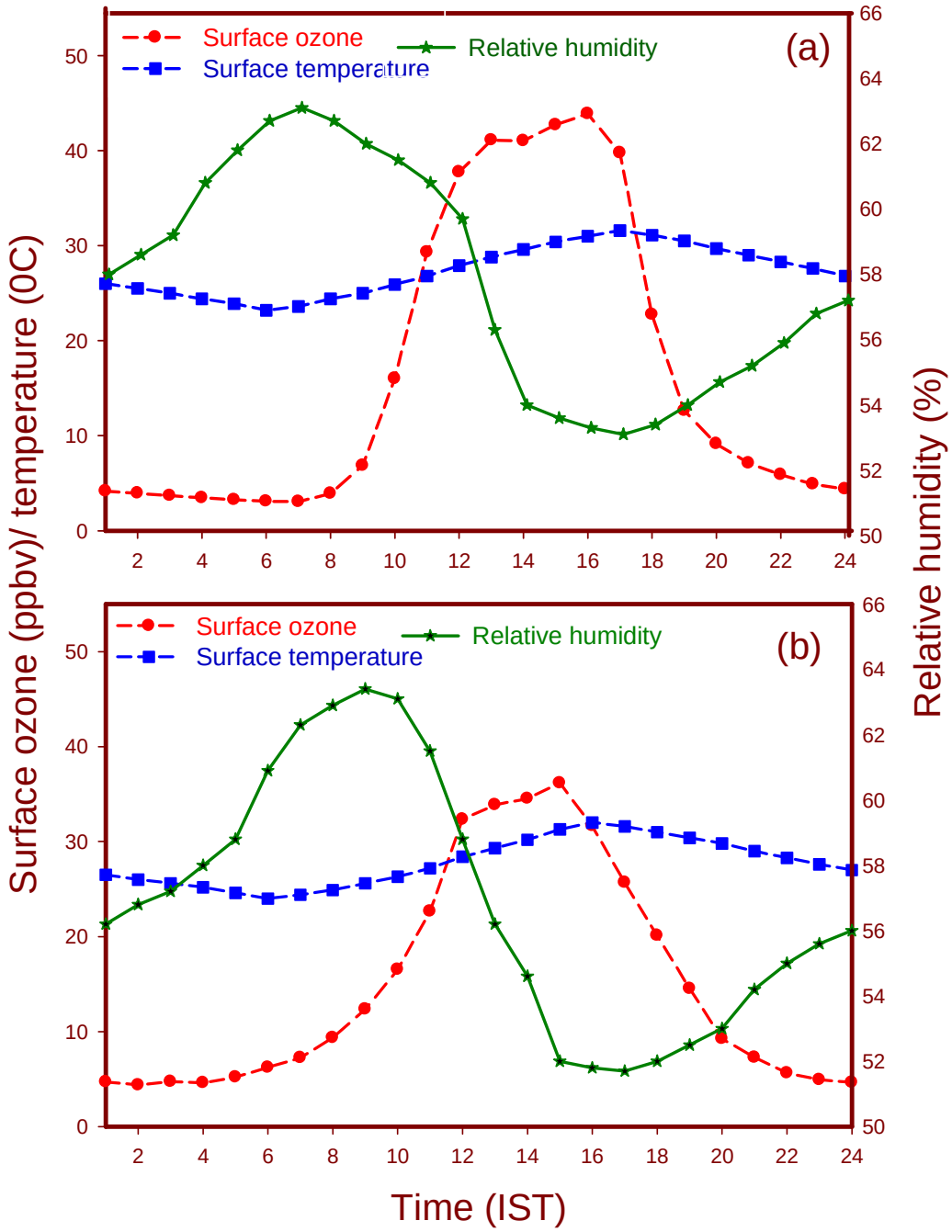

Fig.5.Variation of ozone with temperature and relative humidity at (a) KUC (b) KT during winter season

It is quite significant that NO levels at KT show an increase during morning (06:00 -09:00 h) and evening (16:00-20:00h) hours due to the peak hours of traffic. This elevated level in the concentrations of NO is responsible for the reduction of O_3 at KT. Similarly, the rate of reduction of NO_2* is much higher at KUC during daytime than that at KT. This reduction in NO2* favors

the production of O_3 by photodissociation as governed by R1 and R2. The fast decline of ozone observed at KUC during the late evening hours is attributed to the rapid increase of NO at which titration of O_3 becomes more dominant.

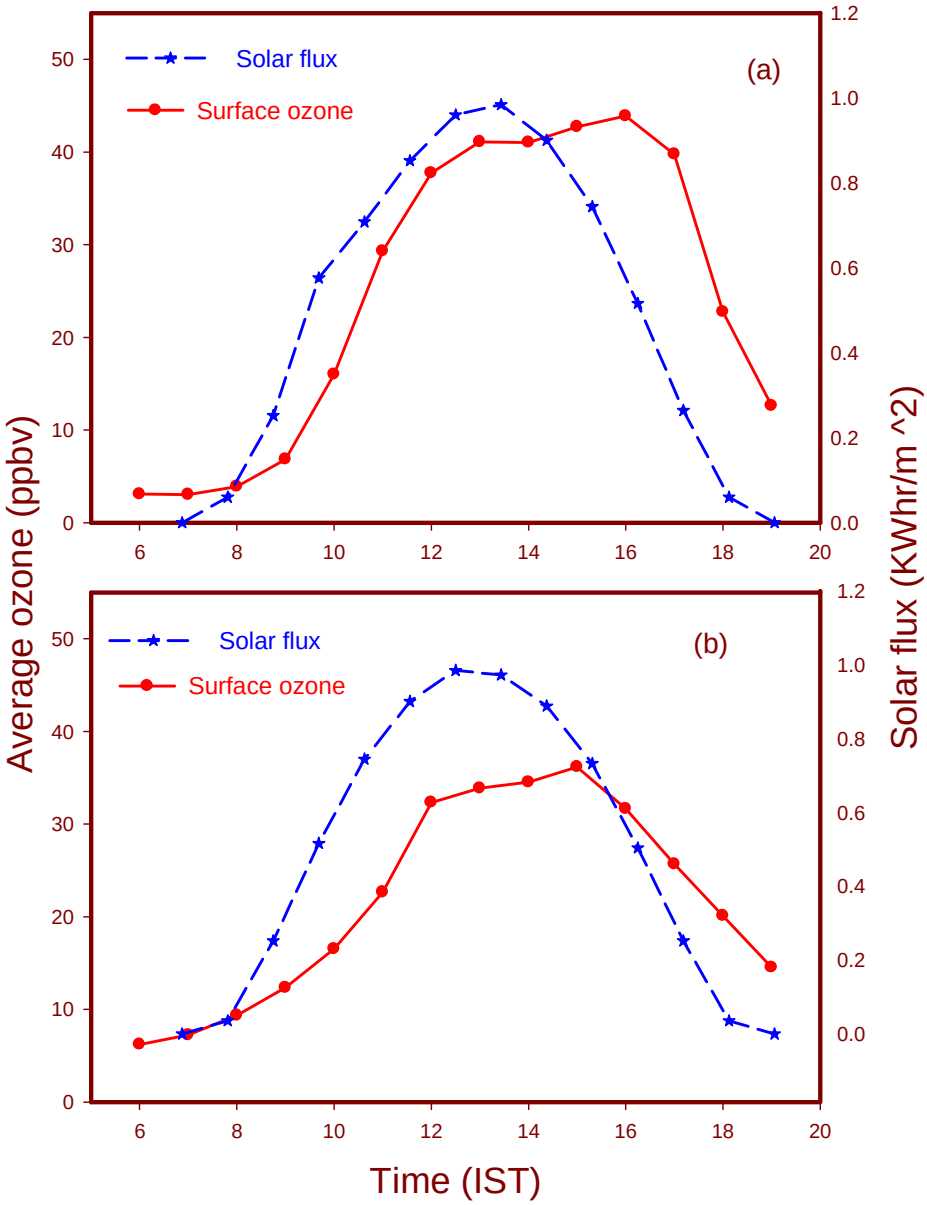

Fig.6.Variation of solar radiation and ozone at (a) KUC and (b) KT

IMPACT OF HUMIDITY AND TEMPERATURE ON OZONE

Comparison between ozone and meteorological parameters like temperature and humidity during winter has been made at KUC. Figure 5 explain the relation between ozone with temperature and humidity at KUC and KT during winter season.

It is evident that ozone variation is directly proportional to temperature and inversely proportional to humidity at these two sites in Kannur. The positive correlation between O_3 and temperature observed is due to the fact that the radiation controls the temperature and hence the photolysis efficiency will be higher during higher photon flux. When the humidity becomes higher, the major photochemical paths for removal of O_3 will be enhanced. Moreover, higher

humidity levels are associated with large cloud cover and atmospheric instability, the photochemical process is slow down and the surface ozone is depleted by deposition on water droplets in this location, hence the O_3 concentration has a strong dependence on humidity. The correlation between O_3 and humidity is more pronounced at KUC since it is a rural location with less amount of pollution. The correlation between surface ozone and solar radiation at KUC and KT is shown the following figure 6.

The correlation coefficient between surface ozone and solar radiation at KUU is 0.94 and that at KT is 0.88. At KUC the ozone concentration peaks after solar radiation attains its maximum value. At KUC, solar radiation reaches its maximum value around 13:00-14:00h, whereas the ozone concentrations reach its high level around 15:00-16:00h.

CONCLUSION

To investigate the difference in the diurnal variability of surface ozone from its precursors, a study has been initiated at Kannur University with the support of the Indian Space Research Organization (ISRO) since November 2009. From the observation, it is found that ozone mixing ratio is higher in KUC, a rural location than at KT, an urban site. The rate of increase and rate of decrease of surface ozone during daytime at these sites are found to be different. Though the NOx variation pattern remains the same, NO_2 is rich in KT due to the heavy pollution raised out of the heavy vehicular activities. The enhanced abundance of NO is responsible for the reduction of ozone at KT, while the relatively small concentration of NO occurs at KUC is the reason for the higher concentration of ozone. It is further revealed that the ozone production has a strong positive correlation to the temperature and has a negative correlation to the relative humidity at these locations. The highest maximum surface ozone concentration observed in winter months at a rural and urban location at Kannur needs further measurements on the production of ozone from VOCs, CO and CH_4 which are quite abundant at these locations and modeling studies to explore the various processes controlling variability of ozone level from its precursors.

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REFERENCES

[1] Debaje and Kakade, *Aerosol and air quality research*, **2006**, 6.4: 444-465
[2] Naja, M., and Lal, S, *J. Geophys.Res*, 107 (D14): 10.1029/2001JD000357, **2002.**
[3] Naja, M., Lal, S., and Chand.D, *Atmos. Environ*., **2003**, 37: 4205-4215.
[4] Nair, P.R., Chand, D., Lal, S., Modh, K.S., Naja, M., Parameswaran, K., Ravindran, S., Venkataramanai, S., *Atmos., Environ.* **2002**, 36: 603-610.
[5] Lal, S., Naja, M., and Subbaraya, B.H, *Atmos. Environ*, **2000,** 34:2713-2724.
[6] Nazeer Ahammed, Y., Reddy, R.R., Rama Gopal, K., Narasimhulu, K.,Baba Basha, D., Siva Sankara Reddy, L., Rao, T.V.R, *Atmospheric Research*, **2006,** 80: 151-164.
[7] Lyons, W.A., Cole, H.S., *J. Appl. Meteorology*, **1976**,15: 733–743.
[8] Levi, II.H., Kasibhatla, P.S., Moxim, W.J., Klonecki, A.A., Hirch, A.I., Oltmans, S.J., and Chameides, M.L, *Geophys. Res. Lett*, **1997**, 24: 791-794.
[9] Londhe, A.L., Jadhav, D.B., Buchunde, P.S., and Kartha, M.J, *Current science,* **2008**, 95: 1724-1729.

[10] Brasseur, G.P, Kiehl, J.T., Muller, J.F, Schneider, T., Granier. C., Tie. X and Haughlustaine.,. *Geophys.Res.Lett*, **1998,** 25: 3807-3820.
[11] Chameides, W.L., Xingsheng, L., Xiaoyan, T., Xiuji, Z., Chao, L., Kiang, C.S., John, J.St., Saylor, R.D., Liu, S.C., Lam, K.S., Wang, T., and Giorgi, F, *Geophys. Res.Lett*, **1999,** 26: 867-870.
[12] Oltmans,S.J., and Levy II.H., Surface ozone measurements from a global network, *Atmos.Environ*, **1994,** 28: 9-24.
[13] Trainer, M., Williams, E.J., Parrish, D.D., Buhr, M.P., Allwine, E.L., Westburg, H.H., Fehsenfeld, F.C., Liu, S.C, *Nature*, **1987**, 329, 705-707.
[14] Rao, T.V.R., Reddy, R.R., Sreenivasalu,R., Peeran, S.G.,Murthy, K.N.V., Ahammed, Y.N., Gopal, K.R., Azeem, P.A., Sreedhar, B., Sunitha, K, *J.Indian Geophys Union*, **2002a,** 3: 151-161.
[15] Rao, T.V.R., Reddy, R.R., Sreenivasalu,R., Peeran, S.G.,Murthy, K.N.V., Ahammed, Y.N., Gopal, K.R., Azeem, P.A., Sreedhar, B., Badarinath, K.S, *J.Indian Geophys. Union*, **2002b**, 3: 163-168.
[16] Winer, A.M., Peters, J.W., Smith, J.P., Pitss Jr., J.N., *Environmental Science and Technology*, **1974**, 8, 1118-1121.