Recent Research in Science and Technology 2010, 2(3): 01–05
ISSN: 2076-5061
www.recent-science.com

PHYSICS

THE SIGNIFICANT ROLE OF CO AND NOx IN THE TROPOSPHERIC OZONE CHEMISTRY

M. K. Satheesh Kumar*, Nishanth. T, K. M. Praseed and Sheela M. Joseph
Department of Atmospheric Science, Kannur University, Kerala 670 567, India

Abstract
Ozone being a greenhouse gas, the chemistry of ozone in the troposphere is considered as an emerging area of investigation after global warming became a reality. The potential role of ozone and its dynamics that changes the atmospheric composition can be retrieved only with the aid of photochemical processes involved in the atmosphere. The various possible chemical reactions that take place at different locations in the atmosphere can significantly change the weather pattern. This is an attempt to review some of the prominent features of the photochemistry of the troposphere and stratosphere.

Key Words: Ozone Chemistry, CO, NOx, SCIAMACHY, MOPITT.

Introduction

The troposphere is the lowest region classified in the atmosphere which has now turn into a section of prominent scientific interest in recent years. This region is highly significant in the atmospheric studies because it contains more than 90% of the entire mass of the atmosphere where intense activity of weather controlling processes is being initiated[1,2]. The troposphere behaves as a chemical reservoir relatively distinct from other layers in the atmosphere. The most energetic wavelengths in the solar radiation are removed within the stratosphere, but light of sufficiently energetic wavelengths penetrates into the troposphere to promote significant photochemical reactions in this region. Subsequently, the photochemistry in this region of the atmosphere has been emerged as a subject of deep concern due to the ozone formation and removal in this region. Tropospheric chemistry is now emerged as a promising scientific tool to analyse the wide range of atmospheric phenomena including Greenhouse effect, Global Warming and Ozone depletion.

Ozone in the troposphere is generated from two major classes of precursors: volatile organic compounds and oxides of nitrogen. Ozone is considered to be a prominent greenhouse gas which has strong absorption in the 9.6 μm and its radioactive forcing efficiency is relatively high compared to all other trace gases [3]. The process of ozone formation is initiated by the reaction of the OH radical with organic molecules and at the same time the ozone is removed from the atmosphere depending on the concentration of trace gases present in the troposphere. Thus the photochemistry that occurs in the troposphere has been emerged as a subject of deep concern all over the world.

Photochemical Oxidation in the Troposphere

Ozone plays a key role in the oxidation chemistry of the troposphere as well as considered to be a vital greenhouse gas. The two main sources of ozone in the troposphere are photochemical production and downward transport from the stratosphere which is rich in ozone [4]. The photolysis of ozone by solar UV radiation shorter than 310 nm leading to the formation of O (^{1}D) atoms. These excited oxygen atom in turn react with water vapor, which is quite abundant in this region, to produce OH radicals. These OH radicals are considered to be powerful oxidants which can initiate oxidation chain reactions [5].

$$O_3 + h\nu\ (\lambda < 310\ nm) \longrightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \longrightarrow 2\,OH$$

Near the earth's surface, ozone is mainly produced by the photochemistry involving pollutants produced by various anthropogenic activities like industrialization, biomass burning, automobile exhausts etc. Owing to the variability in the sources of ozone precursors like CO, CH_4, NOx and VOC, ozone concentration shows large spatial and temporal variations. Considering the rate of increase in the production of these species in the

*Corresponding Author, Phone: 91-09446541575
Email: satheeshmk@gmail.com

atmosphere, ozone chemistry gained wide attention among the researchers in this branch of science.

The simplest carbon containing compound is Carbon monoxide (CO) which is a trace gas in the troposphere mainly produced from the automobiles, partial burning of fossil fuels and industries. The oxidation of CO exhibits many of the key features to discuss the chemistry.

$$CO + OH \longrightarrow H + CO_2$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

$$HO_2 + NO \longrightarrow NO_2 + OH$$

$$NO_2 + hv\ (\lambda < 420nm) \longrightarrow NO + O$$

$$O + O_2 \longrightarrow O_3$$

The net reaction is

$$\mathbf{CO + 2O_2 + hv \longrightarrow CO_2 + O_3}$$

This series involves the presence of NOx and it is evident that the rate of ozone production increases linearly with the concentrations of CO and NOx in the troposphere subjected to the availability of intense sunlight. During night time, in the absence of the sun, NO reacts rapidly with O_3 to get it convert into NO_2 and this NO_2 further oxidizes to produce NO_3.

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

Thus the NO_3 radical produced will undergo photolysis rapidly via two main paths:

$$NO_3 + hv\ (\lambda < 700\ nm) \longrightarrow NO + O_2$$

$$NO_3 + hv\ (\lambda < 580\ nm) \longrightarrow NO_2 + O$$

The possibilities of these reactions rely on the spectral intensity distribution in the solar radiation at a certain location.

Observations

To investigate the significance of the chemistry, an attempt has been initiated to comprehend the impact of the chemistry of ozone in the troposphere by comparing the spatial and temporal variations of ozone and its main precursors CO and NOx at two different locations in India with the aid of satellite data available over these two locations [6, 7, 8]. The two locations selected are, Kannur (11.86 N, 75.35 E), placed in the coastal belt of Arabian Sea in the southern part of India and other Delhi (28.56 N, 77.11E), the capital city of India. Kannur is considered be a small town which is surrounded by vegetation and it is at a height of 10 m from mean sea level. The prominence of this spot is that it is believed to be an unpolluted area whereas Delhi is a polluted city due to the industrial activities and vehicles and this capital city is located at a height of 220 m from mean sea level. Thus the variations in CO and NOx over these two locations would reveal the significant distinctions in the chemistry of the troposphere and a comparison of the chemistry associated within these two regions. The locations of two spots are shown in the map of India in Fig.1.

Figure1. Selected locations of the two spots in India.

Kannur is located very close to the Arabian Sea hence it experiences regular sea-breeze and land-breeze activities. Owing to the temperature contrasts between sea and land, the sea-breeze sets-in about 0800-1000 hours of the day (the Indian local time which is 5.5 hours ahead of GMT) and lasts till late evening up to 1800 hrs. As a result, the sea-breeze transfers air from the marine environment to the land while the land- breeze transports air from the interior land mass. The land breeze is generally weaker compared to sea breeze. The most important meteorological factor is the monsoon rain fall. The south- west monsoon, which sets 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. About 80% of the total annual rain fall occurs from June to November, which constitutes the monsoon season in this state. The pre-monsoon showers occurring in March, April and May caused high degree of convective activities in the atmosphere since this period constitutes the actual summer season. The months of December, January and February are earmarked with insignificant rainfall and low relative humidity and this period is characterized as the winter season.

Fig. 2 shows the tropospheric NO_2 data of Kannur are retrieved from the SCIAMACHY data during 2003-2009 and CO data from MOPITT during 2005-2009.

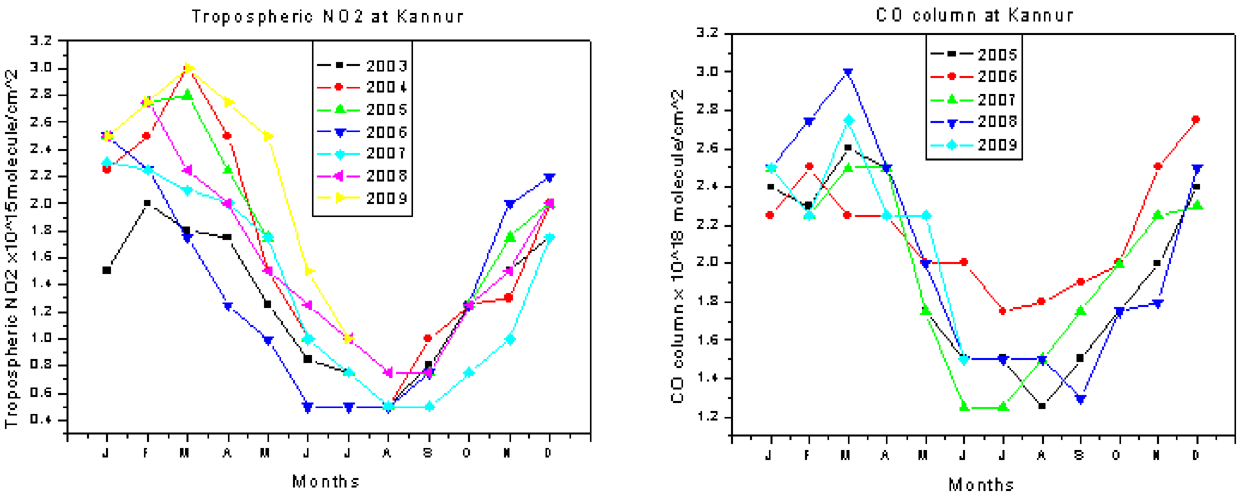

Figure 2. Seasonal variations of tropospheric NO_2 and CO at Kannur (SCIAMACHY and MOPITT).

It shows that the tropospheric NO_2 concentration becomes a maximum in March-April and minimum from June to August every year and this pattern is quite consistent in all the years. The increase in NO_2 is mainly attributed to the enhanced emissions and transport and lightning occurs in the months of October and November. The minimum is mainly due to the severe rainfall occurring in the months from June to August and the acute shortage of solar radiation. However, it shows a rapid increase in the winter season (November – January). This may be due to the decrease in the OH radicals which serve as the detergent in the atmosphere due to the dry weather. The photochemical reactions are more active during this period of time due to the minimum amount of OH radicals. Likewise the CO which is more abundant in Kannur has more or less the same pattern. The increase in the concentrations of CO may be primarily due to the rapid increase in the number of vehicles and the pronounced industrial activities.

Fig.3 shows the variation of NO_2 and CO over Delhi which shows a minimum from July to September regularly every year. But the rapid increase during the winter period in Delhi (November to February) is one of the prominent features. This increase in the NO2 concentrations over the years may be the reason for the photochemical smog being developed in Delhi during winter. The reduction in the OH radical enhances the production of smog and photochemistry of ozone is more significant in Delhi during this period.

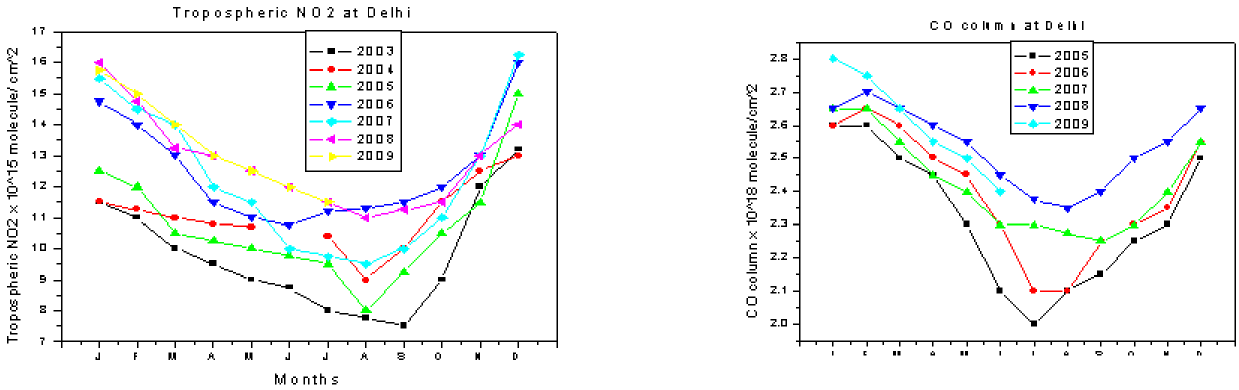

Figure 3. Seasonal variations of tropospheric NO_2 and CO at Delhi (SCIAMACHY and MOPITT)

The increase in the pollution and ozone precursors in both the locations are responsible for the increase in the tropospheric ozone through the photochemical processes. Fig. 4 shows the seasonal variations of tropospheric ozone at these two locations.

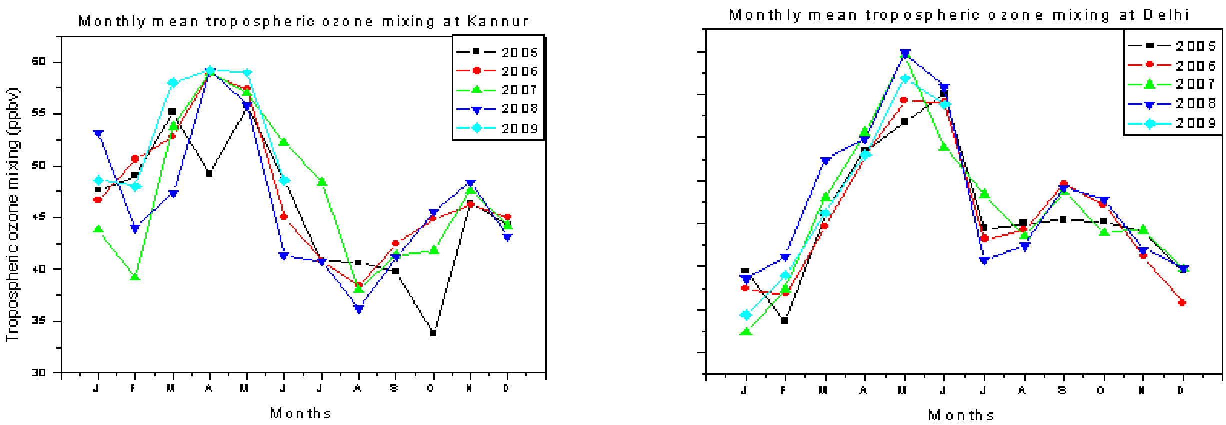

Figure 4. Monthly variations of tropospheric ozone at Kannur and Delhi (TOMS AURA OMI).

The monthly mean ozone values at Kannur show maximum (about 56 ppbv) during April and minimum (about 35 ppbv) in August. Owing to the proximity of the equator and being a coastal site, sharp changes in the climate are not experienced at this location. Surface air temperature, which is a measure of solar insolation, is highest during March and April leading to photochemical production of surface ozone. On the other hand the relative humidity which is higher during the rainy season shows negative correlation with temperature and ozone mixing ratio. The south-west monsoon, which starts by the end of May is quite active during June and July and gets weakened by the middle of August. During October and November months, north- east monsoon prevails. Generally in monsoon period, the sky is relatively overcast, decreasing solar insulation and thereby reducing the photochemical process. Some of the pollutants may be washed out in the rainy season. These factors are the main reasons for the low level of ozone during the monsoon period. But in Delhi, the ozone concentration is relatively high due to extreme temperature in the summer and less humidity. Delhi receives fairly good rain in July-August which is the cause of reduction in ozone. But during the winter month, the ozone concentration grows up due to the photochemical activities. It is further observed that on large number of days the surface ozone values at Delhi is very close to the stipulated WMO ambient air quality standard for ozone (hourly average 80 ppbv), which in turn can bring out health hazard.

Discussion

The tropospheric abundance of ozone and its precursors over Kannur is classified for the first time and they are compared with the standard data recorded at Delhi, the capital city of India. From these observations it is clear that the surface ozone concentrations at these selected spots have a tendency to increase during the period of observation. This is primarily due to the enhancement in the pollution levels. Kannur is relatively less polluted area compared to Delhi due to the extent of intense monsoon activity in this region. However, these observations reveal the fact that the surface ozone would increase if the pattern in the rain fall changes. Thus the change in the monsoon pattern observed during these days in Kannur can intensify the production of surface ozone at this location. This result has the significance that an unpolluted area will have a tendency to become polluted area due to the changes in meteorological parameters at that location. Thus the chemistry of the atmosphere could be analyzed only with the aid of a complete knowledge of the atmospheric parameters. Hence this vital information is essential to open up the way for further investigations using ground based experiments. Thus it is planned to conduct the ground- based observations of diurnal variation of CO, NOx and Ozone in Kannur to retrieve the prominence of the chemistry of ozone in this region.

Summary and conclusion

The increase in ozone and its precursors in this coastal belt is considered to be a serious concern after global warming became a reality. The rapid increase in pollution in this rural area is quite significant in the weather changes. For the last few years it has been observed a variation in change of south west monsoon pattern in Kannur and thereby the shortage of average rainfall. This shortage of rainfall may further increase the pollution over this area, which in turn can enhance the ozone concentration. Thus the variations in atmospheric parameters in this region can change the atmospheric composition remarkably and this may affect climate change over the years.

In this regard, Indian Space Research Organization (ISRO) has succeeded in establishing Environmental observatory in the Geosphere-Biosphere program in selected areas to enhance the grid resolution. Kannur University is one of such centers to conduct ground based observations to monitor trace gases in order to retrieve the chemistry of the atmosphere. Thus analyzing the ground based experimental data and satellite data would enable to unfold the chemistry of ozone over Kannur.

Acknowledgement

This program is initiated under the consistent financial support of ISRO –GBP through their AT-CTM programme. The authors express their gratitude to Kannur University for providing all support to carry out this work. The valuable suggestions rendered by Professor Andreas Richter of University of Bremen, Germany are highly acknowledged. One of the authors (MKS) is highly indebted to the Department of Higher Education, Govt. of Kerala for granting deputation to Kannur University.

References

1. B.H. Subbaraya and Shyam Lal (1998). *Tropospheric Chemistry*, PINSA, 64A (3) 277-288.
2. Shyam Lal, Manish Naja and B.H. Subbaraya (2000). *Seasonal variations in surface ozone and its precursors over an urban site in India*, Atmospheric Environment **34**, 2713-2724.
3. V. Ramanathan (1975) Science, **190**, 50.
4. P.R. Nair, D. Chand, S. Lal et. Al. (2002). *Temporal variations in surface ozone at Thumba (8.6^{0}N 77^{0}E) - a tropical coastal site in India*, Atmospheric Environment, **36**, 603-610.
5. P.J. Crutzen, Lawrence, M. G., Poschi, U., (1999). *On the background photochemistry tropospheric ozone*. Tellus **51**,123-146.
6. K.F. Boersma, H.J. Eskes, J.P. Veefkind, E.J. Brinksma, R.J. van der A, et. al. (2007), *Near-real time retrieval of tropospheric NO_2 from OMI,* Atm. Chem. Phys., 2013-2128.
7. K.P. Heue, A. Richter, T. Wagner, M. Bruns, J. P.Burrows, C. v. et. al. (2005), Validation of SCIAMACHY tropospheric NO2-columns with AMAXDOAS measurements, Atmos. Chem. Phys., 5, 1039-1051.
8. K.P. Bowman (2006). Transport of carbon monoxide from the tropics to the extra tropics. Journal of Geophysical Research-Atmosphere **111,** D02107.