PREFACE

The concentrations of trace gases are low in the atmosphere, but they play a crucial role in determining the ambient air quality over India. Trace gas chemistry can adapt radiative transfer by which it can affect the climate. Ozone ($O_3$) produced in the troposphere plays a vital role in the radiative and chemical processes of the atmosphere due to its strong oxidizing capability. Ozone is an important precursor of hydroxyl radical that decides life time of trace gases species and acts as a major role in the lower atmospheric chemistry. Two mechanisms have been proposed to account for the enhanced rural $O_3$. One is the transport of its precursors like oxides of nitrogen ($NO_x$), carbon monoxide (CO), non-methyl hydrocarbons (NMHCs) followed by the photochemical ozone production and another is transport of $O_3$ from urban areas to the downwind sites. Nitrogen oxide (NO) and nitrogen dioxide ($NO_2$) enter the atmosphere from natural (lightning and biological) processes and pollutant sources. The degradation of ozone reduction is due to the diminishing of solar radiation, affects the photochemical activity and dynamical process in the atmosphere. Photochemical production is nonlinearly dependent on the levels of precursors. Depending upon the precursor's strength and photochemical reactions, tropospheric ozone varies spatially and temporally over the globe. The photochemical ozone production in urban areas rises with $NO_x$ but is less sensitive to volatile organic carbons (VOCs) emissions; in contrast to this in rural areas ozone production is appears to be more sensitive to VOCs emissions. In city areas, the concentration of $O_3$ is usually lower compared to the sub urban areas. This is
mainly because of higher titration process between NO and O$_3$. Meteorological factors are also responsible for the variation of O$_3$ in the ambient air.

Carbon monoxide plays a significant role in the atmosphere on local, regional and global scale, affects air quality. CO is mainly emitted from biomass burning, incomplete combustion of fossil fuel, and oxidation of hydrocarbons released from automobiles and industrial solvents are responsible for about 45% of the total atmospheric CO. The hydroxyl (OH) radical is the primary removal process of CO in the atmosphere. In the troposphere, the reaction between CO and OH represents 90-95% of the CO sink, and about 75% removal of OH. The higher exposure of CO causes impairment of central nervous system functions, changes in cardiac and pulmonary functions, drowsiness, coma, respiratory failure. Sulfur dioxide (SO$_2$) also plays an important role in controlling atmospheric pH as well as atmospheric particle formation. The main sources of SO$_2$ are the injection of volcanic emission, power sector, industrial sector and the transport. In addition, SO$_2$ is involved in the formation of ammonium sulphate, a component of secondary fine particles. The suspected toxicity of SO$_2$ that it may react with oxygen in the presence of water vapor produced sulfuric acid (most acidic among particulate sulphates). Both NOx and SO$_2$ are the main precursors of acid rain, which is hazardous to human health, as well as harmful to plants and animals.

Atmospheric aerosol particles are one of the most variable components of the Earth’s atmosphere and affect the Earth’s radiative balance directly by
absorbing and scattering solar radiation. Also, aerosol particles play a major role in atmospheric chemistry and so affect the densities of other minor atmospheric constituents like ozone. Some aerosol particles contribute to the scattering coefficients which include organic particles, water-soluble inorganic species such as sulphates, nitrates etc. that are produced by conversion from SO₂ and NOx associated mainly with fossil fuel, biomass combustion, ammonium from fertilizers and biological sources. For better understanding on the effect of atmospheric aerosols on climate, visibility and photochemistry, the knowledge of their optical, physical and scattering properties, such as the light extinction coefficient (the sum of the aerosol light scattering and absorption coefficients), single scattering albedo (ratio of scattering to extinction coefficients), mass concentrations and size distribution etc. are required.

The thesis entitled “Investigations on Trace Gases and Its Inter-Comparison with Near Surface Aerosols along with Satellite and Model observations over Semi-Arid Region, India” highlights the inter comparison studies of surface ozone and its precursors with atmospheric aerosols by in-situ and model observations measured at a rural semi-arid site Sri Krishnadevaraya University (SKU) Campus, Anantapur (14.62° N; 77.65° E; 331 m.a.s.l.) situated in southern peninsular India for the period January – December 2012. The present thesis is alienated into six chapters and the depiction on the contents of each of the chapters is discussed below.

Chapter-1 gives a concise introduction to the layers of the atmosphere due to temperature gradients, Chemical composition of the Atmosphere,
atmospheric processes and their roles, photochemical production of O₃, transport of O₃ from the stratosphere, nitrogen dioxides, carbon monoxides and sulfur dioxides in the atmosphere, sources and sinks of trace gases, radiative forcing of atmosphere due to trace gases. Finally, the chapter ends with the discussion of the importance of the present research work, and its future scope to be carried out over this region.

The site description and instrumentation of the various ground-based instruments used for trace gases measurements such as, surface Ozone analyzer (Model APOA-370, HORIBA, Germany), Oxides of nitrogen (HORIBA, APNA-370 Analyzer Germany), carbon monoxide analyzer (Model APMA-370, HORIBA, Germany), Ambient SO₂ analyzer (Model APSA-370, HORIBA, Germany ambient SO₂ monitor, Germany) and Dual Wavelength Aethalometer (Magee Scientific Company, USA) with their measurement techniques, working principles, and methodology followed in analyzing the data are summarized in Chapter-2. In addition, satellite-sensor data were used in the present thesis derived from http://toms.gsfc.nasa.gov/pub/omi/data (TOMS satellite) with a resolution of 0.25° × 0.25°, ftp://jwocky.gsfc.nasa.gov/pub/ccd/ data_monthly_new (OMI satellite) with a resolution of 1° × 1.25° and the data of the BLH (Boundary Layer Height) is retrieved from European Reanalysis Interim Data Products available at (http://data-portal.ecmwf.int). The surface wind flow patterns obtained from NCEP (National Centre for Environmental Prediction) reanalysis data have been used to ascertain the synoptic conditions. The Mini Boundary Layer Mast was used for the measurement of meteorological
parameters such as wind speed, direction, air temperature, relative humidity
and rainfall were discussed along with their technical specifications.

Chapter-3 presents the results of seasonal heterogeneity in surface
ozone and its precursors such as NOx, CO, SO2, regional and local
contribution and source identification by trace gases chemical ratio observed
at Anantapur during January 2012–December 2012. The diurnal mean
maximum concentration of NOx, CO, SO2 was present during morning and
late evenings and lower concentration was found during daytime in respective
of all seasons over measurement site. In contrast, enhanced O3 was present
during daytime and low concentration during early morning and night time.
The seasonal variation in diurnal mean maximum concentration was present
during the summer (48.5±5.4 ppbv) followed by winter (36.7±2.4) and post-
monsoon (34.4±2.7ppbv) and the minimum is observed during the monsoon
(18.2±1.1ppbv). The diurnal mean seasonal variations of maximum NOx, CO,
SO2 were found in winter and minimum in monsoon attributed to
anthropogenic activities, prevailing meteorology and chemical reactions. The
chemical ratio of RSN (SO2/NOx) and slope (Δ [CO]/Δ [NOx]) are strongly
suggested mobile (mainly from vehicular emission) sources are more for
monsoon and post monsoon and significant point source (small industries and
brick making units) contribution for winter and summer. The analysis of O3,
NO and NO2 indicate that the level of oxidant concentration (\([OX] = NO_2 + O_3\))
at a given location is sum of NOx-independent “regional contribution”
(background level of O3) and linearly NOx-dependent “local contribution”.
The results indicated that the dynamics of the boundary layer height is
strongly affected the surface ozone and its precursors concentration over measurement site. The annual mean maximum water vapor content observed in the morning was about 15.4 g m$^{-3}$ and the minimum in the afternoon hours about 13.81 g m$^{-3}$ due to the rapid increase of solar radiation; results elucidated significant effect on production and destruction of O$_3$ and CO. The production rate of O$_3$ strongly depended on UV radiation and found to have good correlation with (R = 0.95) whereas NO$_2$ and CO exhibits anti correlation (R = -0.83 and R= - 0.58). The correlation between CO and O$_3$ is negative (R= 0.69) and slope (-0.54) indicated that local emission of precursors had significant influence on the formation of ozone.

The inter comparison of trace gases and atmospheric aerosols, source identification and comparison study of tropospheric ozone with aerosol optical depth (AOD) were observed at a semi-arid rural site, Anantapur during the period of January 2012-December 2012 were elaborated in Chapter-4. The inverse relation among total aerosol concentration and black carbon (BC) with surface ozone was found to be correlation coefficient (R) of 0.72 and 0.63 respectively. A strong positive correlation has been observed between BC and CO (R=0.71) with an average slope, suggests common or proximate sources likely to be traffic emissions. The annual mean BC/CO ratio was found to be 0.016, while during morning peaks (06:00-09:00 hrs) and evening peaks (18:00-20:00 hrs) about 0.021 and 0.015 respectively at measurement site. The morning BC/CO (0.021) ratio is strongly suggests, fossil fuel is the source of BC and CO during these periods. The diurnal trend of atmospheric visibility was found to be maximum during noon times at around 14:00-16:00 hrs is
about 76 k.m. and minimum 45 k.m during morning period (06:00-08:00 hrs). The negative correlation have been found among SO$_2$, NO$_2$, CO with visibility as $R= -0.80$, -0.53 and 0.72 respectively over the site. The diurnal annual mean variation of scattering coefficient ($\sigma_{sp}$) (at 550 nm), exhibits two peaks, one is at (08:00 hrs) about 90.6±19.4 Mm$^{-1}$ and another is during night time 54±11 Mm$^{-1}$. The positive correlation existed among SO$_2$ and NO$_2$ with scattering coefficients are $R= 0.72$ and 0.64 respectively. The statistical analysis revealed that positive correlation have been found for SO$_2$ ($R=0.79$) and NO$_2$ ($R=0.60$) with single scattering albedo (SSA). This investigation explains the dominance of sulfate particles than the nitrates. They contribute more scattering in this region than nitrates. It is worth to mention that scattering coefficient is found to be decreased during (08:00-12:00 hrs) and SSA is increased which suggests that absorption aerosols like carbonaceous particles diluted at a greater speed than the scattering particles. The diurnal variation of BC370/BC880 and delta $-$C (BC 370-BC 880) indicates during morning hours clear organic component presence in atmospheric aerosols and the dominance of fossil fuel generated BC during night and day times. Characterization of the aerosol properties shows biomass burning aerosols and continental aerosols are dominant over the site especially in winter. The satellite data was used to compare the measurement site tropospheric ozone with the other sites in India and the variation of AOD at measurement site.

An impact of aerosol loading on surface ozone and photolysis rates by in-situ and model observations were discussed in **Chapter-5**. Tropospheric Ultraviolet Visible (TUV) radiative transfer model with a 4-stream discrete
ordinates radiative transfer solver is used to calculate the Photolysis rate coefficients i.e., j-values. NCAR Master Mechanism (NCAR-MM), a chemical box model (zero dimension), developed at National Center for Atmospheric Research, Boulder, USA, has been used to simulate the diurnal variation of O₃, CO and sensitivity analysis. For the aerosol impact on surface ozone and photolysis rates, we run the model without aerosol optical depth (absence of aerosols) and taken it as base run. The set of simulations is made by keeping all input parameters constant at the values of base run and varies only AOD from 0.5 to 2. The model result shows that the extremely high aerosol concentration over the measurement location has a very strong impact on photo chemical activities and ozone formation. The correlation between aerosol and ozone concentrations appears in a linear nature. The O₃ concentration is very sensitive to aerosol loading when aerosol loading is high, and this sensitivity is reduced when aerosol loading reaches to low. In order to evaluate the total column ozone effect on J(O₃), a sensitivity test was performed. The analysis shows that the increase in the total column ozone causes the decrease in the J(O₃) due to the spectral actinic flux around 300 nm decreases for increasing total ozone. The effect of water vapor on surface ozone has been studied and analyzed by model observation.

Chapter -6 summarizes the main conclusions of the study and sketches out the scope for future research based on the results discussed in the thesis.

Finally some of the important results quoted (indicated by ‘*’ mark) in the thesis have been published in the peer-reviewed journals as given below.
Research publications


Y., Shyam Lal, 2012. Analysis of Diurnal and Seasonal behavior of Surface Ozone and Its Precursors (NOx) at a Semi-Arid Rural Site in Southern India. *Aerosol and air Quality Research* 12, 1081-1094.

**Seminars/Conferences**

1. Participated and presented a paper in the IITM-WMO Seminar on “Metropolitan Air Quality Forecasting and Services (SAFER) on 30\textsuperscript{th} April 2013 and International workshop on “Changing Chemistry in Changing Climate: Monsoon” (C4) during 1\textsuperscript{st}-3\textsuperscript{rd} May 2013 held at IITM, Pune, India.

2. Participated and presented in the Two-Day National workshop on “Emerging Trends in Condensed Matter Physics” held at Govt. First Grade College Bettampady, Puttur Taluk during 5\textsuperscript{th} and 6\textsuperscript{th} September, 2013.

3. Participated and presented a paper in the Indian Aerosol Science and Technology Association, IASTA-2012 held at Mumbai during 11-13\textsuperscript{th} December 2012.

4. Participated and presented a paper in two day national conference on “Facing Challenges on Climate Change: Earth and Atmospheric Systems” (FCCC-2012) held at S.K. University, Anantapur during 30\textsuperscript{th} -31\textsuperscript{st} October 2012.

5. Participated and presented a paper in the workshop on “Frontiers of Atmospheric Physics and Technology” held at Yogi Vemana University, Kadapa from 01\textsuperscript{st} -03\textsuperscript{rd} March 2012.
6. Participated in the “Board of Research in Nuclear Sciences (BRNS) third school on Analytical Chemistry” (SAC-2012) organized by Department of Chemistry, S.K. University, Anantapur during 24\textsuperscript{th} Feb-01\textsuperscript{st} March.

7. Participated and presented a paper in the two day national workshop on “Environmental Pollution and Impacts on Public health and Agriculture” (EPPA) held at Sri Krishnadevaraya University, Anantapur during 21\textsuperscript{st} -22\textsuperscript{nd} Feb 2012.

8. Participated and presented a paper in the 17\textsuperscript{th} National Space Science Symposium (NSSS-2012) held at Sri Venkateswara University, Anantapur during 14\textsuperscript{th} -17\textsuperscript{th} Feb 2012.

9. Participated in the national workshop on “Environmental Degradation and Management” held at S.K. University, Anantapur during 22\textsuperscript{nd} -23\textsuperscript{rd} September 2011.