The diurnal and seasonal variations of Ozone and its precursors such as CO, SO\textsubscript{2} and NO\textsubscript{x} are measured by in-situ measurements and inter compared these results with near surface aerosols such as black carbon, total aerosol concentration, visibility, single scattering albedo and scattering coefficient and important results are found by model simulation at Anantapur for the period from January 2012 to December 2012. UV radiation, water vapor, Boundary layer dynamics, local meteorology and atmospheric chemistry played a vital role in the changes observed over the measurement location. The important findings of the present study are discussed below.

The diurnal O\textsubscript{3} profile showed, a declined peak in the morning (07:00-09:00 hrs), which is attributed to O\textsubscript{3} titration with freshly emitted NO. After 09:00 hrs, O\textsubscript{3} concentration gradually increases to reach a maximum value at 14:00 hrs (48±4.2 ppbv) in the afternoon and due to its photochemical formation through the photolysis of NO\textsubscript{2} shown in the following set of reactions. This increase is strongly supported by the highest intensity of UV radiation observed during those hours while different trace gas precursors are getting mixed up in the mixed layer. The low concentration of O\textsubscript{3} observed at night was due to the absence of photo chemical oxidation and titration with NO in the residual boundary layer. The diurnal NO\textsubscript{x} exhibited a double wave peak with distinct peaks during morning hours (06:00-08:00 hrs) and others at night (20:00-22:00 hrs). The morning peak was higher in magnitude than the night peak. During morning hours between 06:00 and 08:00, the NO\textsubscript{x} concentrations at the observation site increased rapidly, which was due to the
increased emissions of motor vehicles, industrial activities and also atmospheric dynamics. The freshly emitted NO could react with O$_3$ without solar radiation and produce more NO$_2$ and reduce O$_3$ concentrations. This increased peak in summer was mainly attributed to the availability of more intense solar radiation, well mixing of precursors with mixed layer. The significant concentrations of O$_3$ observed in winter was attributed to a lower mixing height that results in trapping of pollutants near the earth’s surface and favourable wind flow from high pollutant sources. These seasonal variations can be attributed to changes in synoptic wind patterns, prevailing air mass type and seasonal differences in meteorology. Local and regional contributions to oxidants revealed that during nighttime, NO$_x$-dependent (local) contribution was more compared to daytime was mainly attributed to high emission of NO$_2$ from heavy duty diesel trucks. The diurnal variation OX showed similar to the variation of O$_3$. It showed a mid-day peak and lower nighttime concentrations. The concentrations of NO, NO$_2$ and NO$_x$ were higher on weekdays (WD), while an opposite trend was observed in the case of (OX) where concentrations were lower during weekdays.

High levels of CO during morning and late evening over the study region attributed to combined effects of anthropogenic emissions, boundary layer processes, chemistry as well as local sources and wind patterns. The high mixing ratio of CO was present during the night time, owing to the boundary layer descends and remains low until early morning, leads resisting the mixing of anthropogenic emissions with the upper layer. In the absence of human
activities, atmospheric CO was controlled by the balance of photochemical production and destruction through the reaction with OH. The concentration of CO was very low during the monsoon months (July–September) can be ascribed to the large amount of precipitation prevailed, high wind velocities, and change in general wind direction. The temporal variation of SO$_2$ had a more similar pattern to NO$_2$ rather than to NO and NOx, suggested that SO$_2$ and NO$_2$ have common sources. In all seasons SO$_2$ showed bimodal distribution; morning peak owing to traffic related pollution and an evening peak which reflects possibly a combination of traffic and some local anthropogenic activities. Studies on wind speed and wind direction over measurement site are carried out by using the NOAA Earth system Research Laboratory NCEP/NCAR reanalysis data showed that during the post monsoon, winds were predominantly from the easterly or north easterly and central Indian regions that are reported to be the potential source region for pollutants. The diurnal averaged monthly mean maximum water vapor was observed in October (18 g m$^{-3}$) and a minimum in March (9.4 g m$^{-3}$), due to solar radiation. The huge amounts of precipitation reduce atmospheric pollution via associated wet deposition processes. In contrast, a lack of precipitation during the winter months reduces the potential for wet deposition and results higher concentrations. The annual mean ABL height increased from (8:00 hrs) about 740m, and reached the maximum at (14:00 hrs) was about 2289 m and lower height found during mid nights was about 340m over study region. The maximum and minimum ABL were found in the summer at
14:00 hrs (3007 m) and in the winter at around 05:00 hrs (150 m). The seasonal diurnal mean ABL was found to be shallower during the winter (840 m) and post monsoon (856 m) and as compared with the summer (1216 m) and monsoon (1106 m) observations. The lower concentration during morning can be attributed to less UV radiation, leads lower photolysis rates and titration with its precursors and meteorology. The enhancement of surface ozone during noon times mainly depends on the photolysis which is in the range of 315-420 nm (UV-A). This seasonal variation of $O_3$ followed the seasonal variation of UV radiation, i.e. maximum in the summer (23.5±2.4) and followed by the winter (19.8±2.2), post monsoon (19.3±2.1) and minimum in the monsoon (18.6±1.9) W/m$^2$.

The investigations elucidated, the diurnal variation of NO$_2$ that has the exactly opposite pattern with the diurnal UV radiation with strong negative correlation coefficient (R= - 0.78). The diurnal trend of atmospheric visibility was found to be maximum during noon times at around (14:00-16:00 hrs) about 76 k.m. and minimum during morning periods (06:00-08:00 hrs) about 45 k.m. The diurnal variation mainly attributed to anthropogenic emissions, boundary layer processes, chemistry as well as local sources and wind patterns. The seasonal maximum visibility was observed in the monsoon (93.7 k.m) and followed by the summer (80.2 k.m) and minimum was found in the post monsoon and winter (28.1 and 40 k.m).

We also reported that Air chemistry data can provide valuable information on the sources of pollutants measured at a site. The temporal
lower and higher RSN values are the representative of the local contribution and regional contribution over the site. The seasonal mean RSN for monsoon, post monsoon, winter and summer are 0.16, 0.32, 0.54 and 0.49 respectively, elucidated local contributions were more for monsoon and post monsoon and significant regional contribution for winter and summer. The ratio of concentrations of SO$_2$ to NOx (RSN) was used to determine the source of pollutant emissions. The seasonal mean RSN for monsoon, post monsoon, winter and summer are 0.16, 0.32, 0.54 and 0.49 respectively, elucidated mobile (mainly from vehicular emission) sources were more for monsoon and post monsoon and significant point source (small industries and brick making units) contribution for winter and summer. An interesting feature has been found in this analysis is an obvious enhancement of SO$_2$/NOx during the periods of significant O$_3$ peaks. The chemical species ratio suggested that there is a significant relation between O$_3$ and S/N ratio and the mixing ratio of ozone was strongly depended on regional contribution. The local and regional contribution to oxidants also suggested that regional contribution was more during winter and summer over measurement site. The slope ($\Delta$ [CO]/$\Delta$ [NOx]) and intercept for monsoon, post monsoon, winter, summer were 21.3, 16.5, 8.2, 10.6 and 7.2, 105.1, 254, 61.1 respectively. The comparatively higher slope values of monsoon and post-monsoon data suggested that during these seasons the majority of CO and NOx are produced from area-wide sources i.e. vehicles. The comparatively lower slope values of winter and
summer suggested that significant point sources contribution over the site during these periods.

A comparative study was also made by using a satellite data over the observation site on the monthly mean variations of near-surface ozone, tropospheric ozone, tropospheric NO₂ and total ozone. The monthly mean near surface ozone and tropospheric ozone are revealed that two are having similar variations with low values from June through September and increasing trend was observed from December onward, reached peak observed in summer months (April). The monthly mean variation of tropospheric NO₂ exhibited similar to tropospheric ozone. Moreover a positive correlation between tropospheric ozone and tropospheric NO₂ is clear visible in the scatter plot in with a correlation coefficient of 0.80. The monthly mean variation of total ozone showed opposite pattern to the tropospheric and surface ozone variations. A comparative study has been made by using the MLS and OMI satellite data for the study period from January to December 2012; found that the high mean tropospheric O₃ was over Delhi. Low tropospheric O₃ was observed in the winter in Delhi and Pune. This was mainly attributed to less solar radiation during this season. Compared with the southern locations such as Anantapur and Hyderabad, Delhi has enhanced values due to less biomass burning/ anthropogenic activities, hotter and humid climate lead to lower concentration over the southern locations.
The monthly BC distribution profile showed high values in November (3.82 ± 0.31 µg m^{-3}) and December (3.84 ± 0.32 µg m^{-3}). Minimum BC values are observed in May (0.94 ± 0.12 µg m^{-3}) and August (0.95 ± 0.13 µg m^{-3}) due to wet surface deposition by rain. October showed sudden raise in amplitude due to change in WD and seasonal transition. Results showed that the minimum O_3 values correspond to maximum values of BC aerosols. This generally happened at 07:00 hrs local time, a period characterized by windless condition and less stratified boundary layer. For these transition hours, the measurements show a build-up of BC while ozone is titrated away by the reaction with NO. Recent studies indicated that BC aerosols may interact heterogeneously with O_3 and its precursors to influence O_3 variability, NOx/HNO_3 ratio and HOx balance in the atmosphere. This reduction value of surface ozone at Anantapur was somewhat high compared to Hyderabad (3.5 µgm^{-3}). This reduction was due to the aggregate structure of soot particles, which offer a large specific area for heterogeneous interactions with relative trace gases like ozone. The statistical analysis showed that positive relation between black carbon and oxides of nitrogen. The analysis are suggested that aerosols can increase the NOx concentration, this mainly attributed to the heterogeneous reactions between NO and HNO_3 adsorbed on BC surface may contribute to “renoxification” through the production of HONO. The diurnal variation of BC and PM_{2.5} was similar indicating similar sources and formation mechanisms for them. The monthly mean ratio of BC/PM10 showed maximum was found in December (0.28) and minimum was in May.
(0.05). While maximum of BC/ PM$_{2.5}$ was found in October (0.36) and lowest was found in May (0.09). Winter had the highest fraction (~22%) of PM10 mass whereas the lowest fraction (~0.08%) was found in summer. The seasonal pattern of BC/ PM$_{2.5}$ suggested maximum was found in post monsoon (~35%) and minimum was in summer (~ 0.13), due to coarse mode particles were dominated in the summer. PM$_{10}$ values are found to be high around 23.64±2.53 μg m$^{-3}$ during the winter period, with low values (16.82±1.73) occurring during the monsoon months. Besides meteorological conditions like high air pressure, atmospheric stability and temperature inversion also had played their active role in affecting their concentration during the winter season.

Particulate matters have complex effects on solar actinic flux photolysis rates in the troposphere and at the surface. Total aerosol concentration ($M_T$) influences the tropospheric trace gas chemistry by its surface reaction. A negative correlation was obtained for daily mean values of aerosol and O$_3$ concentration during the study period. Surface ozone reduction was significant during winter by aerosol loading compare with other seasons, can be due to lower temperature act as catalyst for heterogeneity chemistry between aerosols and trace gases. This reduction could be due to the aggregate structure of aerosol particles, which provides a large specific surface area for heterogeneous interactions with reactive trace gases such as O$_3$. The result showed that besides metrological effects, high aerosol loadings have played a significant impact on UV flux. The diurnal cycle of UV flux and aerosol
concentration strongly suggested that a negative has been presented between them with correlation coefficient of 0.86. A strong positive correlation has been observed between BC and CO (R=0.71), suggested common or proximate sources likely to be traffic emissions. Hence, BC and CO are good indicators of fossil fuel combustion and biomass burning at the site. 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 ratio strongly suggested, fossil fuel was the source of BC and CO during these periods. The diurnal annual mean variation of $\sigma_{sp}$ (at 550 nm) showed 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 large values of $\sigma_{sp}$ during morning are due to the severe emission of particulate pollutants from morning traffic rush hours. In addition, the low wind speeds and low solar heating in the morning favour a rather low boundary layer height that caused a huge particle loading near the surface and therefore high values of $\sigma_{sp}$. The result showed that positive correlation existed among SO$_2$ and NO$_2$ with scattering coefficient as R= 0.72 and 0.64 respectively. The investigations strongly supported that sulfates have higher scattering scenery than nitrates over the study site. The diurnal patterns of CO and scattering coefficients have the similar pattern and have positive correlation (R=0.75). In contrast, surface ozone had the opposite pattern with scattering coefficient, owing to produce from precursors such as methane and non methyl hydrocarbons in the presence of sufficient oxides of nitrogen.
The single scattering albedo showed an evident diurnal pattern with two maxima, one in the morning at around (03:00 hrs) about 0.82 and one in the evening (12:00 hrs) about 0.81. These high values of SSA reveal relative increases in contribution by scattering aerosol types. The statistical analysis revealed that positive correlation existed among SO$_2$ (R=0.79) and NO$_2$ (R=0.60) with SSA. These investigations suggested, sulfate particles are the higher scattering particles than the nitrates. The aerosol scattering albedo found in the surface boundary layer at measurement site is below the 0.86 that reveals the shift from cooling to warming, i.e. absorption particles are dominated over the site. A significant positive correlation was found between PM$_{2.5}$ and BC with correlation coefficient of R=0.84, suggested black carbon particles were significant contributors to fine mode particle concentration. While, the positive correlation has been found for CO, SO$_2$ and NO$_2$ with correlation coefficients R=0.69, 0.52 and 0.72 respectively, suggesting fine mode particles are emitted from the sources of CO, SO$_2$ and NO$_2$. Additionally, the fine and ultrafine fractions of the ambient PM include the primary and secondary acidic sulfates and nitrates, which are produced through both homogeneous and heterogeneous processes. BC showed a strong correlation with NO$_2$ (R = 0.78 and 0.80) during the winter and summer. This, together with the strong BC–CO correlation, is further evidence that the significant source of BC is transport-related. A moderate correlation (R=0.53) has been found for BC and NO$_2$ in the monsoon. The poor correlations between BC and SO$_2$ have been found for the monsoon, winter and summer.
(R=0.41, 0.48 and 0.25 respectively) suggest these two are emitted from different sources and low levels of SO\textsubscript{2} indicate less number of sources have found in adjacent areas. The diurnal mean ratio of BC (370 nm) and BC (880 nm) was presented and was found to more than unity (>1.0) at around (06:00-08:00) in winter indicating a clear organic component in atmospheric aerosols. The lower unity values were found during day time and night time except morning hours (06:00-08:00) indicates the dominance of fossil fuel generated BC at the site. The main source locally producing BC is the road close to the site, where emissions from vehicles exhausts can diffuse over the area of interest. During the winter we found that significant greater and lower than the unity values, suggested both biomass burning and fossil fuel burning were the contributors to BC. The interesting feature has been found during March 15 to April 10 (>1.0), which indicated the presence of biomass burning smoke into the atmosphere, might be due to agricultural and grass land burnings are more in this period. The lower than the unity values are found during May, indicated fossil fuel burning was dominant for BC production. The results indicated that Delta-C values positive during morning hours (06:00–08:00 hrs) and negative during day time and night time except morning (06:00–08:00 hrs). A positive value during morning hours indicates the presence of biomass burning smoke (UV enhanced organic species) into the atmosphere where as negative values can occur due to fossil fuel burning.

The monthly mean maximum AOD was noticed in summer (0.39) and post- monsoon period (0.33). The monthly mean AOD during the monsoon
was 0.27, which is mainly attributed to most of the aerosol concentration washed out by rainfall. And low monthly mean AOD was noticed in the winter (0.23). A positive correlation was observed between tropospheric ozone and AOD with correlation coefficient \( R = 0.60 \).

The Tropospheric Ultraviolet-Visible, TUV model version 4.2, is used to calculate spectral actinic flux and photolysis rates for each molecule of interest, taking the interaction between aerosol particles and radiation into account for cloud less conditions. The maximum photolysis rates are found in winter and lower was found in summer is mainly due to effect of the natural variation of columnar ozone and abundance absorbing aerosols are dominant during these period. For the summer simulation we considered only March and April months, this period have high burning activities (SSA is 0.6). The maximum photolysis rates \( J(O_3) \) about 2.89E-05 and \( J(NO_2) \) about 7.47E-03 was found at maximum UV radiation (38 W/m\(^2\)) in noon hours (01:00 hrs). The statistical analysis suggested that a strong positive correlation (\( R=0.96 \) and 0.99) was found to \( J(O_3) \) and \( J(NO_2) \) with UV radiation. The diurnal \( J(NO_2) \) profile, \( J(NO_2) \) starts from morning 06:00 hrs was about 1.32 E-07 s\(^{-1}\), due to less solar radiation. During the day time the photolysis rate of NO\(_2\) increases and attained maximum at around 12:00 hrs was about 8.94 E-03 s\(^{-1}\), after onwards gradually decreases with declined solar radiation.

The modeled \( O_3 \) pattern is well correlated to the observed diurnal variation. The deviation between the observed and the modified \( O_3 \) are due to the assumptions/approximations inherent in the model. In this case model
estimation is fair in agreement with the observed ones. The correlation coefficient is quite satisfactory. The results from model simulation showed that summer has maximum concentration followed by winter and less concentration was observed in the monsoon period. This seasonal variations pattern exactly coincided with the observed seasonal variation. The model produced only morning peak, not able to produce secondary peak in model simulation of CO. Over all, simulated CO is not good correlated with the observed variation. This disagreement might be attributed with the two things; 1) CO is not a secondary pollutant 2) some other radical data is not incorporated in the simulation. Chemical box model is based on reaction chemistry and it produces output data through chemical reactions only. From the model results, it is clearly known that the high aerosol loading over measurement location has strong impact on surface ozone formation. In the model simulation when we considered AOD is 1.5 and 2, the mean values of surface ozone decreases with 22% and 24% of base run ozone mean value respectively. The sensitivity calculations are shows that the calculated ozone decreased with the increases of aerosol loadings. The change of ozone concentrations with aerosol loadings appear in non-linearity behaviour over measurement site. The model was simulated with same gas phase chemistry and changes in RH from 50% to 99% to understand the water vapor effect on surface ozone. The model simulation resulted the diurnal variation of ozone was decreases with increased water vapor. The surface ozone was decreased by 3.2% at 50% of RH, and it is increased by 12.4% at 99% of RH. We
concluded by this model analysis higher water vapor content in the lower atmosphere has played a significant role in ozone destruction.

To analyze the impact of the changes in AOD on photolysis frequencies, the change in $J(O_3)$ above the ground level (500m) with aerosols and $J(O_3)$ without aerosols are simulated. The set of simulations is made by keeping all input parameters constant at the values of base run and varies only AOD from 0 to 2. We found that the calculated $J(O_3)$ and $J(NO_2)$ are decreased with enhancement of aerosol loading. The change in $J(O_3)$ and $J(NO_2)$ with aerosol loading were appeared in non-linearity behavior. This sensitivity of $J(O_3)$ on total column ozone showed that the statistically significant decreasing trend in $J(O_3)$ can be attributed mainly to the corresponding increasing trend of total ozone. This is mainly due to the spectral actinic flux around 300 nm decreases for increasing total ozone.