3.1 Introduction

The concentrations of trace gases are low in the atmosphere, but they play a crucial role in determining the ambient air quality over a location. Moreover, trace gas chemistry can adapt radiative transfer by which it can affect the climate. Air pollution is one of the main environmental problems in urban and rural areas, particularly in megacities. The rapid growing urbanization will cause wide ranging potential consequences for environmental problems. Ozone is an important precursor of hydroxyl radical that decides life time of trace gases species and plays a key role in the lower atmospheric chemistry. The relationship between O$_3$ and its precursors represents one of the major scientific challenges associated with urban air pollution (Gabusi et al., 2005). Ozone is a strong oxidizer in the atmosphere and its chemistry is complex. The surface ozone (O$_3$) is a secondary pollutant which is not directly emitted into the atmosphere but is formed from the complex mixture of precursors. Surface ozone is formed because of the interactions of nitrogen oxides (NOx=NO+NO$_2$) and non-methane organic compounds in the presence of solar radiation. The reduction in the solar radiation affects the photo chemical activity and dynamical process in the atmosphere. Photo chemical 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 (Saraf et al., 2004). The photo chemical ozone production in urban areas rises
3.2 Diurnal variations of O₃ and NOₓ

The annual diurnal variations of O₃ concentration are presented in Fig. 1 (a). In the diurnal O₃ profile, a declined peak is observed in the morning (07:00-09:00 hrs), which is attributed to O₃ titration with freshly emitted NO. After 09:00 hrs, O₃ 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 NO₂ shown in the following set of reactions.

\[
\text{NO}_2 + h\nu (\lambda< 420 \text{ nm}) \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

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 increase in O₃ mixing ratio in day time is mainly because of the photo oxidation of anthropogenic hydrocarbons, carbon monoxide and methane in the presence of sufficient amount of NOₓ. (Nair et al., 2002; Reddy et al., 2008(b)). The low concentration of O₃ observed at night is due to the absence of photo chemical oxidation and titration with NO in the residual boundary layer shown in the following titration reaction.

\[
\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2
\]

The night time variations of O₃ concentration are probably due to the difference in reactivity of O₃ with NO, VOCs in different meteorological,
environmental and dispersion conditions. The annual average surface level concentrations of NO, NO₂, NOₓ and O₃ in the study area were 1.7±0.1 ppbv, 3.6±0.5 ppbv, 5.2±0.6 ppbv and 35.1±3.15 ppbv respectively, during the sampling period. The concentrations of NO and O₃ were higher during daytime while opposite trends existed for NO₂ and NOₓ. This is mainly attributed to the photochemical reactions of NOₓ, O₃ and the balance between the emissions (natural and anthropogenic) and the mixing processes of both horizontal and vertical convections.

The diurnal NOₓ 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) as shown in Fig 1(b). The morning peak is higher in magnitude than the night peak. The morning peak of NO₂ and NO appears in the same hour and the O₃ peak appears 6 hours after NO and 5 hours after NO₂ peak. The difference in time is attributed to the time taken for conversion of NO to NO₂ involving NMHCs. During morning hours between 06:00 and 08:00, the NOₓ concentrations at the observation site increased rapidly, which is due to the increased emissions of motor vehicles, industrial activities and also atmospheric dynamics. The freshly emitted NO could react with O₃ without solar radiation and produce more NO₂ and reduce O₃ concentrations. In the afternoon, NOₓ concentrations decline, due to an increase in downward solar flux which initiates photo chemical reactions and the results being O₃ domination by the conversion of NO₂ to NO. The concentration of NO at night time gets oxidised to NO₂ and then NO₃ radicals (Atkinsin et al., 2000). After
mid night the NOx concentration decreases due to formation of dinitrogen pentoxide ($N_2O_5$) and less anthropogenic activities. The formation of $N_2O_5$ is in equilibrium with NO$_3$ and NO$_2$ by the following reactions.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(3.4)}
\]

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(3.5)}
\]

\[
\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(3.6)}
\]

The dissociation of $N_2O_5$ in day time has to produce NO$_3$, NO and O ($^3P$).

\[
N_2O_5 + h\nu \rightarrow \text{NO}_3 + \text{NO} + \text{O} \quad \text{($^3P$)} \quad \text{(3.7)}
\]

During the day time the following titrations increase the availability of NO, NO$_2$ in the atmosphere for photo oxidation and O$_3$ titration.

\[
\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2 \quad \text{(3.8)}
\]

\[
\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \quad \text{(3.9)}
\]

Particularly during the day time the oxidation of NO produces NO$_2$ which contributed to the amount of O$_3$ at this station. Finally at night, the NOx and O$_3$ were maintained quickly. Since there was no solar radiation, both the source emission and dilution effects decreased significantly.

Similar diurnal patterns were observed in many urban and rural areas all over the world (Han et al., 2011; kumar et al., 2010; Lal et al., 2000; Ahammed et al., 2006) for O$_3$ and NOx. Sometimes the change in the variations of pattern were also observed because of local air circulations or short term meteorology effects (Coastabile et al., 2007; Pudasinee et al., 2006), but the basic pattern always remained the same. The concentrations
may vary in different environments depending upon the background air pollution, specific emission conditions and general meteorological conditions.

**Fig. 1.** Diurnal variation of (a) O$_3$ and (b) oxides of nitrogen NO, NO$_2$, NOx over Anantapur during the study period.
3.3 Seasonal variations in O$_3$ and NO$_x$

The monthly mean O$_3$ concentrations are shown in the form of 3D surface contour plot in Fig. 2(a). It is observed that the variation of O$_3$ for all seasons shows the similar diurnal pattern. The monthly mean maximum and minimum O$_3$ are observed in March (55.7 ppbv) and August (16.5 ppbv) for the study period. For seasonal variation diurnal mean maximum concentration was present in summer (48.5±5.4 ppbv) followed by winter (36.7±2.4) and post monsoon (34.4±2.7ppbv), while the minimum in the monsoon (18.2±1.1ppbv). This increased peak in summer is 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 is 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 (Nishanth et al., 2012). The low concentrations of ozone received during the monsoon are due to insufficient sunshine for photochemical production, high relative humidity and rain washout process. These seasonal variations can be attributed to changes in synoptic wind patterns, prevailing air mass type and seasonal differences in meteorology. From these results it is evident that surface O$_3$ exhibits a strong seasonal variation and the meteorological parameters have a strong impact on the study location.

The maximum and minimum concentrations of NOx observed during the period of study were 20±3.2 ppbv and 0.9±0.1 ppbv in January and May respectively (Fig.2 (b)).The maximum /minimum magnitudes of average
observed of NOx concentration are 6.0±0.6/ 3.1±0.4 ppbv respectively in winter and in the monsoon. The average concentrations of NO\textsubscript{X} for the post-monsoon and summer are 5.7±0.5 ppbv and 5.0±0.6 ppbv respectively. Thus the concentration of NOx shows a small seasonal variation. NOx mixing ratios are generally stronger in the early morning and at night in all the seasons. The minimum and maximum observed mixing ratios of NOx were 3.2 ppbv, 19 ppbv in winter, 2.0 ppbv, 11 ppbv in summer, 2.3 ppbv, 4.3 ppbv in the monsoon and 2.9 ppbv, 10.7 ppbv in the post-monsoon. NO\textsubscript{x} higher levels attained in winter (19.2±2.3 ppbv) and summer (11.2±1.3 ppbv) as they got transported by favourable wind from the polluted regions.
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The low level of NOx in the monsoon is due to the intense cloud formation and rain washout of pollutant precursors. These seasonal changes are attributed to the change in climate, long range transport, natural and anthropogenic activities and to O3 sensitivity to VOC/NOx ratio.

### 3.4 Local and regional contributions to oxidant concentration

The mean variations in daytime and nighttime values of oxidant concentrations ([OX] = O3 + NO2) are shown in Fig.3. It is possible to consider that the [OX] at a given location has a NOx-independent, and a NOx-
dependent contributions. The former is effectively a regional contribution which equates to the regional background of [O₃] level, whereas the latter is effectively a local contribution which correlates with the level of primary pollution. Due to the influence of the photochemical reactions on the formation of [OX], differences should be arising between values observed during daytime and nighttime.

During nighttime, NOₓ-dependent (local) contribution is more compared to daytime is mainly attributed to high emission of NO₂ from heavy duty diesel trucks over the observation site. The data also indicate that the regional contribution to the oxidant depends on the wind direction. The slope of the relationship between [OX] and [NOₓ] representative of the local contribution to the oxidant concentration and the value of [OX] when [NOₓ] = 0 representative of the regional contribution to the oxidant concentration.

Based on the photostationary state, it is possible to infer an expected variation in daytime mean [NO₂]/[OX] values with [NOₓ]. This variation is shown in Fig.4 along with the fitted empirical expression. The data shows that a progressively greater proportion of [OX] is in the form of NO₂ as the level of NOₓ increases. Low level ratios of [NO₂]/[OX] due to the high concentration of O₃ during daytime. On the other hand, during nighttime it is expected the complete conversion of NO and O₃ to NO₂.

If photochemical processes have an influence on [OX] levels in polluted areas, then a difference between the behavior of [OX] during daytime and nighttime would be expected. Fig.5 shows the diurnal variations of mean
values of [OX] concentration. This variation is similar to the variation of [O₃]. It shows a mid-day peak and lower nighttime concentrations. The [OX] slowly rises after sunrise, reaches a maximum during day, and then decrease until the next morning. This is due to photochemical O₃ formation. Hence we suggest that the [OX] level at this site was less influenced by NOₓ emissions.

![Graph showing variation of daytime and night time mean values of OX with level of NOₓ.](image)

**Fig. 3.** Variation of daytime (top panel) and night time (bottom panel) mean values of OX with level of NOₓ.
Fig. 4. Variation of daytime (left panel) and nighttime (right panel) mean values of \([\text{NO}_2]/[\text{OX}]\) with the levels of \([\text{NO}_x]\).
3.5 Weekday and weekend analysis

In order to investigate the weekday-weekend analysis over the measurements site, the authors divided the total sampling period into two parts: weekdays (WD, Monday-Friday) and weekends (WE, Saturday and Sunday). NO\textsubscript{x} showed a difference in both weekdays and weekends. Compared with weekends (WE), the concentrations of NO, NO\textsubscript{2} and NO\textsubscript{x} were higher on weekdays (WD), while an opposite trend was observed in the case of [OX] where concentrations were lower during weekdays (Fig.6). This is in consistence with the results obtained from the earlier studies carried out in other locations as reported by Han et al., 2011, Qin et al., 2004(a) and Song et al., 2011. This variation is mainly due to characteristics features of the experimental site, e.g. variations in direct emissions of NO\textsubscript{2} owing to

![Diurnal variation of average [OX] (oxidant concentration) values during observation period.](image-url)
variations in local driving conditions or vehicular fleet composition; local sources of biogenic hydrocarbons which can amplify photochemically induced NO to NO$_2$ conversion under VOC limited conditions and overnight accumulation of free radical precursors. The output from diesel vehicles daily running on the nearby national highways, not only contains more NO$_X$ generally, but also likely to have a higher proportion of the NO$_X$ as NO$_2$ (Clapp and Jenkin 2001). In addition, the average diurnal variation on weekdays was greater for NO than for NO$_2$. This is because NO$_2$ has a longer lifetime than the more reactive NO (Debaje and Kakade, 2006). Fig.6 also shows that daily variation of the mean values of the NO$_X$ and [OX] levels during weekdays and weekends. The average maximum value of [OX] at weekends was higher than weekdays. This type of temporal variability presented here can also be found in other cities (Mayer, 1999).
3.6 Diurnal and Monthly variation of CO

Figure 7 shows the average diurnal variations of CO for different months and results suggest a bimodal distribution with peaks at 7:00–09:00 and 18:00–20:00 hrs. The concentrations of CO start decreases from morning peak to afternoon and attains low peak at around 12:00-13:00 hrs in all seasons. The morning peak dominates the evening peak except for the monsoon. 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. It is important to note that the major anthropogenic sources for CO over site are fossil fuel burning, solid waste burning and biogenic emissions. The diurnal variation with low concentration during day could partly be attributed to changes in the synoptic conditions.

**Fig. 6.** Diurnal variation of mean values of [NO], [NO₂] (top panel) and [NOₓ], [OX] (bottom panel) for weekdays and weekends.
circulation of the wind. In order to sustain the high ozone values during the noon time, large amounts of precursors are needed. This leads the low values of precursors during noon period. Besides the anthropogenic activities, the diurnal variation of air pollutants was pronouncedly influenced by the change of planetary boundary layer (PBL). 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 is controlled by the balance of photochemical production and destruction through the reaction with OH. (Novelli et al., 1998). Apart from the direct emissions, the only chemical source of CO is the formaldehyde (HCHO). The observed mixing ratio of CO exhibited clear seasonal variability. The monthly mean maximum and minimum of CO are found in January (317±12 ppbv) and July (51±2 ppbv) respectively. The monthly mean maximum mixing ratio was observed in May, owing to high anthropogenic emissions from road construction near to measurement site. The materials used to lay down the road contribute more amount of CO. For seasonal variation maximum concentration was present in the winter (310±17 ppbv) followed by the summer (180±21 ppbv) and post monsoon (174±20 ppbv), while the minimum in the monsoon (72±9 ppbv). The concentration of CO in the post-monsoon was higher than the pre-monsoon. The concentration of CO is 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 large amounts of precipitation reduced atmospheric pollution via associated wet deposition processes. Further, wind velocities will allow for pollutant transport away from sources; increase mixing processes with the winds coming from the marine. The marine air was characterized by lower concentration of CO, resulted minimum levels during the monsoon. Low temperature and solar radiation, chemical reactions slow down, and emission and dynamic transport processes are expected to have a bigger influence on the diurnal variations of the gases in the winter. Additionally, a lack of precipitation in the winter months reduces the potential for wet deposition and associated cleansing mechanisms.

![Monthly variation of CO over Anantapur](image)

**Fig.7.** Monthly variation of CO over Anantapur.
On the other hand local winds also play a significant role for enhancement of CO in the winter due to their being transported through south easterly wind flow from the polluted regions. Conversely, during the summer months, the average PBL height is typically at its greatest, resulting in increased mixing through a greater volume of the troposphere air and hence causing dilution of the pollutants. Moreover, the availability of enhanced OH during the summer months may also act to consume CO. The lifetime of CO is relatively long (~1 to 3 months or longer) with respect to synoptic time scale (~4 days), the seasonal change in lifetime has little impact on ambient CO level near source regions (Holloway et al., 2000).

### 3.7 Diurnal and Monthly variation of NO\textsubscript{2} and SO\textsubscript{2}

The diurnal variation of NO\textsubscript{2} exhibited a double peak pattern with two distinct peaks (Fig. 8); one is in the morning (07:00-08:00 hrs) and the other at night (20:00-22:00 hrs). Between 06:00-08:00 hrs, NO concentrations attained maximum because of increase in heavy-duty diesel truck activities, a significant source of NO emissions. During the morning hours, sunlight begins to induce a series of photochemical reactions, NO is converted to NO\textsubscript{2} via a reaction with O\textsubscript{3}. NO is mainly produced by motor vehicles and its lifetime is short due to its reaction activity, and NO\textsubscript{2} can be produced by biomass burning besides automobiles. NO is a primary contaminant, whereas O\textsubscript{3} and a large percentage of NO\textsubscript{2} are secondary contaminants, formed through a set of complex reactions. However NO to NO\textsubscript{2} oxidation processes will determine how NOx is subsequently partitioned between NO and NO\textsubscript{2}. It is
well known that the sunlight initiated, free radical catalysed degradation of VOC in the presence of the NOx leads to the oxidation of NO to NO₂ (Jenkin and Clemitshaw, 2000). Other possible NOx-dependent sources of OX may derive from the emission of species that can lead to NO to NO₂ conversion. Two potential gases are the formaldehyde (HCHO) and nitrous acid (HONO) are emitted from vehicles exhausts and they are photo labile and may therefore lead to the generation of free radicals. These radicals play a key role in NO to NO₂ conversion during daytime. The rate of the oxidation is strongly dependent on the NO concentration and it is much more rapid at the elevated levels of NO, usually verified close to the sources. Therefore, it is probable, that some NO to NO₂ conversion occurs immediately after emission and before the reaction is effectively halted (or at least significantly reduced in rate) by dilution. The measured NO₂/NOx ratio is a convenient variable of the extent and completeness of atmospheric oxidation processes. The seasonal mean NO₂/NOx ratios for the monsoon, post monsoon, winter and summer were about 0.88, 0.91, 0.76 and 0.80 respectively, indicating a higher conversion of NO to NO₂ over the measurement site. During the day time hours, increase in downward solar flux initiates a series of photochemical reactions between several precursors resulting in formation of O₃ by the conversion of NO₂ to NO as a result of photolysis. Besides these chemical reactions, another factor that influences air-pollutant concentrations is the height of the mixing layer over the measurement site and results low concentration during afternoon. During the late evenings NO₂ concentration
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gradually increases and reaches to a peak value at around (20:00 hrs) are attributed to emissions from heavy vehicular traffic and weak vertical diffusion in the boundary layer. After the midnight NO$_2$ is reduced due to decrease in traffic emissions, and formation of dinitrogen pentoxide (N$_2$O$_5$) (Atkinson, 2000). The air mass from the surrounding areas can also contributes to local NO$_2$ concentrations, so the transport and local emission may be the reasons why NO$_2$ concentration is more over the study region.

The temporal variation of SO$_2$ had a more similar pattern to NO$_2$ (Fig.9) rather than to NO and NOx, suggesting that SO$_2$ and NO$_2$ have common sources. In all seasons SO$_2$ shows 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. The major source of SO$_2$ over the measurement site is brick making units; they are located north easterly to the site. The morning phenomena are suggestive of fumigation peaks, which arose after the post-sunrise decay of the surface temperature inversion. However, the possibility of a relationship to the small industrial cycle and traffic peak cannot be ignored. Increase in oxidation of SO$_2$ during daytime due to higher ambient temperature might have lead to lower SO$_2$ mixing ratio. The lower afternoon SO$_2$ levels are attributed to the dilution of ambient SO$_2$ concentrations owing to the midday growth of the mixing layer in conjunction with a decreased traffic density compared to rush hour times (Reche et al., 2011). After the late evening peak, the SO$_2$
concentration remains comparatively low throughout the night because of increase of wind speed and inversion remains through the whole night.

The monthly diurnal mean values of SO$_2$ and NO$_2$ are shown in (Fig. 9, 8). The results show that concentrations of gaseous compounds were highly dynamic with significant seasonal variations characterized by high winter and low monsoon levels. The average NO$_2$ concentration in the monsoon, winter and summer were $(2.6 \pm 0.2 \text{ ppbv})$, $(4.08 \pm 0.4 \text{ ppbv})$ and $(4.03 \pm 0.4 \text{ ppbv})$ respectively. The concentration of NO$_2$ did not show significant variation during the period of observation at this site but only had a small seasonal variation. The monthly mean SO$_2$ mixing ratio was observed significantly low $(0.46 \pm 0.02 \text{ ppbv})$ in the monsoon and high $(2.42 \pm 0.21 \text{ ppbv})$ in the winter. During the monsoons, low pollutant concentrations can be ascribed to precipitation driven washout and polluted air mixes well with the clean marine boundary air causing dilution of the pollutants. Consequently, during the winter months, increased atmospheric stability and less atmospheric circulation makes the air mass more stagnant. Additionally, lack of precipitation during the winter reduces the potential for wet deposition and associated cleansing mechanisms. The daily and monthly variations of these species in a rural atmosphere are mainly affected by the transport processes, photochemical activity and the diurnal–nocturnal evolution of the planetary boundary layer (Adame et al., 2012). The seasonal trend described is mainly due to the following: 1) poor winter atmospheric dispersion conditions with stable inversion layer and relative low wind speed influence seasonal pollutant
levels. 2) Traffic and small industrial process emissions and meteorology. The major source of oxides of nitrogen is vehicular emissions over the site. The similar results were reported by Hao and Wang (2005), pointed out that 74% of ground NOx originates from vehicular emissions, power plants and industrial processes. The similar results of gaseous pollutants i.e. higher concentrations in the summer and lower mixing ratios in the monsoon were reported by Suqin Han et al., 2013; Nishanth et al., 2012; Yonghong Wang et al., 2013 were attributed to a combination of meteorological conditions and photochemical activity of the region.

**Fig.8.** Monthly variation of NO$_2$. 

![Monthly variation of NO$_2$](image)
3.8 Effect of meteorology on pollutant concentration

The levels of CO, SO$_2$ and NO$_2$ are not only influenced by local emissions, meteorology, urban effects and trans-boundary transport in the lower troposphere. The meteorological parameters that are expected to affect CO, SO$_2$ and NO$_2$ in many urban and rural areas are ambient temperature, wind speed, wind direction, mixing height and inversion layer. The mixing height plays key role for pollutant level, defined as the height at which vertical mixing takes place (Manju et al., 2002). Seasonal variations on meteorology can affect the transportation of air pollutants. Particularly, wind direction and wind speed can cause serious changes on the direction of plume. The inverse
relationship among CO, SO$_2$ and NO$_2$ concentrations is the wind speed which shows predominant influence on local sources in which strong winds flush the pollutants out of the site whereas low winds allow pollution level to increase. The CO-wind relation varies with the season and magnitude of the wind and the mixing ratio of CO decreases with the increasing wind speed. The higher concentrations of NO$_2$ and CO during the post monsoon and summer may be due to their being transported through south westerly wind flow from the polluted regions (Fig.10).

**Fig.10.** Distributions of hourly wind speed and wind direction in different seasons.
It was observed that when ambient temperature goes down and humidity goes up SO$_2$ mixing ratio increases and vice versa. The relationship between SO$_2$ mixing ratio and ambient temperature are more prominent in diurnal cycle of SO$_2$ mixing ratio in the winter. SO$_2$ mixing ratio shows a significant negative correlation with rainfall and Relative humidity.

**Fig.11.** Mean prevailing winds at 850 hpa over Indian region during monsoon, post monsoon, winter and summer (from NCEP/NCAR reanalysis data).

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 for all seasons, for assessing possible transport of pollutants from different regions. The colour contour indicates the wind speed (m/s) and arrows indicate the wind direction. During the monsoon
period westerly winds with greater speed were found to be dominant that were coming from the marine region i.e. from the Arabian Sea, having no pollutants and results sharp decrease over the site (Fig.11). 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. These features were responsible for the observed high concentrations of CO, SO$_2$ during the post-monsoon season.

Similar results had been reported by Latha and Badarinath, 2003 and Safai et al., 2007. Sulphur dioxide is a reactive gas and it will eventually be converted into sulphuric acid in the atmosphere. The transport time will be sufficient for SO$_2$ conversion, even the emission source is far away to the measurement site. Hence, regional transport also played an important role for the enhancement of SO$_2$ over site, because of low emission sources are found at measurement site.

3.9 Effect of Water vapor content on surface ozone, oxides of nitrogen and CO concentration

The atmosphere is an oxidizing medium and many environmental trace gases are removed by oxidation from the atmosphere. Water vapour is the most an important trace species in the lower atmosphere; it is actively participated in atmospheric chemical reactions. Surface ozone and OH are the strong oxidizing agents in the lower atmosphere. They play a vital role in the formation of radicals in the atmosphere. The main chemical reaction of water vapour is the production of OH radicals in the lower atmosphere. The
production rate of OH radical mainly depends on water vapour content in the lower atmosphere. Photolysis of O\textsubscript{3} produces O (\textsuperscript{1}D) that reacts with H\textsubscript{2}O producing OH radicals, and results depletion of O\textsubscript{3} (Pitts and Pitts, 2000).

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O (}\textsuperscript{1}\text{D}) \tag{3.10}
\]

\[
\text{O (}\textsuperscript{1}\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} \tag{3.11}
\]

The near surface water vapour content is calculated from the relative humidity (RH) and temperature (T) of the surface measurements, using the empirical relation given by (Kneizys et al., 1980).

\[
\rho_s = A \exp(18.9766 - 14.9595 A - 2.4388A^2) \tag{3.12}
\]

\[
A = \frac{T_o}{(T_o + t)}
\]

\[
T = T_o + t
\]

\[
\rho_v = \rho_s \cdot \left(\frac{\text{RH}}{100}\right) \cdot [1 - (1 - \frac{\text{RH}}{100}) \cdot (\rho_s \cdot \frac{\text{R}_v \cdot T}{P})]^{-1}
\]

Where \(\rho_v\) is the estimated water vapour content and \(\rho_s\) is the saturation density of water vapor at \(T_o = 273.15\) K, \(R_v\) is the gas constant for water vapor \((4.615 \times 10^{-3}\) mbar g m\(^{-3}\) K\(^{-1}\)), \(t\) is temperature in °C, and \(P\) is the total pressure in mbar.

Water vapor content in the atmosphere plays a crucial role in the production and destruction of ozone. Diurnal variation of ozone over the measurement location is mainly due to 1) photochemical reactions involving precursor gases depending on the oxides of nitrogen and solar radiation and 2) loss mechanism involving OH radicals. The annual mean maximum water vapor content observed in the morning (07:00-08:00 h) was about 15.4 g m\(^{-3}\) and the minimum in the afternoon hours (01:00-02:00 h) about 13.81 g m\(^{-3}\).
due to the rapid increase of solar radiation (Fig. 12). After 16:00 h water vapor gradually increases till late night. The increase in water vapour is significant for the night time chemistry. Another important reaction of OH, is its reaction with NO₂ to produce HNO₃ at night.

The surface ozone concentration decreased during the early morning hours in the study area for which one of the possible reasons being high water vapour content present this period. Heterogeneous chemistry has assigned greater role for the particle and gas phase reactions. High water vapour content acts as a catalyst for this heterogeneous chemistry in the shallow boundary layer. This chemistry leads the reduction of ozone to its surface reactions. The surface ozone is very sensitive to aerosol loading (Bian et al., 2007; Li et al., 2011; Reddy et al., 2011; Suresh Kumar Reddy et al., 2012). During the same period, the results show that NOx concentration is more in the measurement site. One of the possibilities for NOx enhancement is, aerosols increase in the NOx concentration. The simulation by Tang et al., 2003 reported that aerosols can increase NOx concentration by 40% by reducing its photolytic loss in spring over the north western Pacific. High aerosol concentration can reduce the photolysis frequency and reduce the surface ozone concentration (Bian et al., 2007; Li et al., 2011). Water vapor and surface ozone have opposite patterns where as oxides of nitrogen had the same pattern (Fig. 12). The surface ozone is negatively correlated, by the contrast oxides of nitrogen are positively correlated with water vapor for majority of the days during the study period. (Nair et al., 2011; Suresh Kumar Reddy et al., 2012).
Fig. 12. The diurnal variation of mean O₃, NOx and water vapor.

Fig. 13. Monthly mean variation of O₃, NOx and water vapor content.
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 maximum temperature was observed in March at the sampling site. The highest monthly average water vapour noticed in the monsoon and post-monsoon, were about 16.5 and 16.8 g m\(^{-3}\) respectively. Water vapour during winter was (14 g m\(^{-3}\)) and a minimum was observed in summer (12.9 g m\(^{-3}\)). As noticed in the Fig.13, significant water vapor content was observed in winter which led to high concentration of oxides of nitrogen. It is evident from the Figs 12 and 13 that the increase of \(\rho_v\) is associated with the decrease in ozone in the atmosphere. The low value of water vapor \(\rho_v\) content observed in summer is one of the possible reasons for the enhanced surface ozone in summer.

The water vapour content in the atmosphere plays a key role in the formation and destruction of CO. The annual mean diurnal variation of CO shows two peaks one is during morning and another is at late evenings and decline peak during noon, mainly attributed to 1) natural and anthropogenic sources and photochemical reactions 2) OH radicals. In the absence of anthropogenic activity, atmospheric CO is controlled by the balance of photochemical production and destruction through the reactions of CO with OH.

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{H} + \text{CO}_2 \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{H}_2\text{O}_2 + \text{M}
\end{align*}
\]
Reaction with the hydroxyl radicals (OH) is the primary sink of CO in the lower atmosphere. The reaction between CO and OH represents 90-95% of the CO sink (Novalli et al., 1998).

The major chemical loss of CO is by reaction with OH radical during daytime. During night time, HCHO accumulates, while during the morning its chemical reaction and photo dissociation results in production of high CO during the early hours. Hence, apart from the direct emissions, the only chemical source of CO is the formaldehyde (HCHO). Seasonal mean magnitude of $\rho_v$ and CO was about 12.9 g m$^{-3}$ and 172 ppbv in the summer; 16.5 g m$^{-3}$ and 72 ppbv in the monsoon; 16.8 g m$^{-3}$ and 195 ppbv in the post-monsoon and 14 g m$^{-3}$ and 300 ppbv in the winter, respectively (Fig. 14). The minimum CO levels might also be caused by the availability of enhanced OH

**Fig.14.** Monthly mean variation of CO and water vapor content.

The major chemical loss of CO is by reaction with OH radical during daytime. During night time, HCHO accumulates, while during the morning its chemical reaction and photo dissociation results in production of high CO during the early hours. Hence, apart from the direct emissions, the only chemical source of CO is the formaldehyde (HCHO). Seasonal mean magnitude of $\rho_v$ and CO was about 12.9 g m$^{-3}$ and 172 ppbv in the summer; 16.5 g m$^{-3}$ and 72 ppbv in the monsoon; 16.8 g m$^{-3}$ and 195 ppbv in the post-monsoon and 14 g m$^{-3}$ and 300 ppbv in the winter, respectively (Fig. 14). The minimum CO levels might also be caused by the availability of enhanced OH
during the summer months. The monsoons bring large amount of precipitation, high wind velocities, and changes in general wind direction over the measurement site. 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.

3.10 Structure of the atmospheric boundary layer (ABL) and impact on trace gases

The data of the BLH (Boundary Layer Height) was retrieved from European Reanalysis Interim Data Products available at (http://data-portal.ecmwf.int). It gives data at only three hourly intervals, so we considered only every three hours data for diurnal variation. The ABL plays an important role in the dilution and elimination of pollutants, and can be considered as one of the factors determining pollution potential over a region of interest. Atmospheric boundary layer is a part of troposphere, where a vertical mixing of pollutants occurs. The most two important meteorological parameters are: the ABL and wind speed. The boundary layer height indicates the vertical diluted ability of air pollutants, and the wind speed represents the horizontal ventilation, which benefits the dispersion of air pollution. The diurnal variation of ABL showed a similar trend in all the seasons. 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 (Fig.15) over study region. After the sunrise the
thermals gradually lift the inversion base, thereby increasing the depth of the ABL. This is favourable for increased mixing of the atmospheric constituents in the mixed layer and a subsequent redistribution of constituents in a greater atmospheric volume. ABL is controlled by solar radiation, orography, wind and moisture content. The deepening of the ABL, and the associated convective turbulence thoroughly mix and redistribute pollutants in this period. Boundary layer is convectively very active and eddies mix the temperature, moisture and aerosols called as mixed layer during day time. Surface air temperature decreased before sunset and residual layer (contains remaining previous days well mixed layer air) has higher temperature than the lower layer and leads temperature inversion, played a crucial role in changing the boundary layer. The thermals stop after the sunset and mixed layer deforms to a shallow stable boundary layer near the surface and a residual layer in the air separated by an inversion in potential temperature, inhibiting vertical transport of pollutants. The temperature inversion is considered as a perfect reflector of air pollution. Generally, a surface-based inversion associated with radiation cooling occurs during night and its thickness gradually increases to the maximum at mid night with the minimum wind speed. After the sunrise the thermals are strengthened and break the night time inversion. The ABL greatly varied during 8:00–19:00 hrs, while it seemed to be unchangeable during 20:00–7:00 hrs. The ABL has the good correlation coefficient (R=0.76) with solar radiation during daytime, while it was mainly
correlated with wind speed during night time (R=0.42). This result suggests the boundary layer height has influenced by different essential factors.

![Graph showing diurnal mean annual variation of Boundary layer height](image)

**Fig. 15.** Diurnal mean annual variation of Boundary layer height for the observation period.

The result shows that low ozone concentration and enhanced peak of nitrogen oxides are mainly due to lower boundary layer heights in the early morning. This reduces the mixing process between the ozone poor surface layer and ozone rich upper layer and contributes to reduction of ozone. The diurnal variation of pollutants (CO, NOx, SO\(_2\)) shows two peaks one is at morning and another at late evenings. The primary morning peak might be associated with anthropogenic activities and fumigation effect in the boundary layer, which brings pollutants from the nocturnal residual layer shortly after the sunrise (Stull, 1988). The pollutant concentration was found to be lower during noon, and is mainly attributed to increased solar heating leads to
increase turbulent effects and a deeper boundary layer, leading to faster dispersion of pollutants and hence a dilution of pollutants concentration occurs near to the surface. The expansion of boundary layer height is causing constant mixing of warmer lighter surface air with the upper cold air. The secondary evening peak of pollutants concentration can be coupled with the stable meteorology and the low nocturnal boundary layer, reduced the ventilation effects and confined the pollutants caused the secondary peak during night time. Such a stable boundary layer during night prevents plumes emitted from tall point sources from reaching the surface and therefore does not affect the surface air quality. Therefore, the diurnal variation of pollutant concentration has a strong association with the local boundary layer dynamics over measurement site.

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 (150m) (Fig. 16). The seasonal diurnal mean ABL was found to be shallower during the winter (840m) and post monsoon (856 m) and as compared with the summer (1216 m) and monsoon (1106 m) observations. The lower CO concentration in the monsoon can be attributed to turbulent weather conditions and insufficient formation of inversion. In contrast, in the post monsoon the inversion gradually climbs the pressure level, results less boundary layer and results accumulation of pollutants. The higher CO concentrations in the winter due to the highest pressure level pertaining to the lowest mixing height which results in a very quiet weather condition and does not allow escaping of the pollutants
into the atmosphere, results in higher accumulation of pollutants near surface in this season. This can also be one of the prime reasons for higher concentration of CO concentration in the winter. Increasing surface temperatures, wind speed and convective activity during the summer, are responsible for dispersion of the pollutants and leads to the boundary layer deepens, thus lowering the CO concentrations. This suggests that the pollutant dispersion is minimum in the winter, and also maximum mixing of pollutants occurs in the summer. Negative relationship (R= -0.59) has been found between CO and ABL was seen with higher values in the winter and lower in the monsoon and summer.

![Fig. 16. Monthly mean variations of CO and Boundary layer height.](image)

The monthly mean maximum ABL observed was in the month of April (1186 m) when CO was 123 ppbv; however, lowered ABL in the month of
November (676 m) caused higher CO (298 ppbv). Seasonal mean magnitude of ABL and CO was about 1216 m and 172 ppbv in the summer; 1106 m and 72 ppbv in the monsoon; 856 m and 195 ppbv in the post-monsoon and 842 m and 300 ppbv in the winter, respectively. Pollutant dispersion is weaker during the lower boundary layer heights and these observations strongly suggested the diurnal and seasonal variations of CO have strongly depended on boundary layer dynamics.

3.11 An effect of UV radiation on trace gases

The diurnal and seasonal variability of UV (ultraviolet) radiation reaching the earth’s surface is governed by astronomical and geographical parameters as well as by the atmospheric conditions. Although UV radiation reaching the earth’s surface constitutes only a small fraction of the total radiant solar energy, understanding ultraviolet radiation characteristics is very important, because it has important impact on atmospheric chemistry. UV radiation plays an important role in the troposphere and stratosphere through its photo chemical reactions. In the lower atmosphere surface ozone is a secondary pollutant and highly depended on the photo dissociation process of its precursors. The production rate of ozone depends on UV radiation. The production and destruction of ozone depends on the UV- A and UV- B radiations respectively. The destruction ozone was present at noon times by UV radiation leads to the production of electronically excited O (\(^{1}\text{D}\)) atom, which consequently reacts with H\(_2\)O to form OH.

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O} (^{1}\text{D}) \quad (<320\text{nm})
\]
The diurnal variation of surface ozone and nitrogen dioxide strongly depends on the UV radiation. The diurnal annual mean enhancement mixing ratio of ozone was present at around (16:00 hrs) about 47±3.2 ppbv and lower concentrations at (07:00 hrs) about 15.8±1.7 ppbv (Fig. 17). 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 315-420nm (UV-A).

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \left( \text{^3P} \right) \quad \text{where} \ \text{hv} < 420 \text{ nm}
\]

\[
\text{O} \left( \text{^3P} \right) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

The diurnal variation of ozone exactly followed by the diurnal variation of UV radiation, and suggests that it is strongly depended on UV radiation. The seasonal maximum ozone was observed in the summer (48±5.9) and followed by the winter (36±2.4), post monsoon (34.4±2.1) and minimum in the monsoon (18.2±1.1 ppbv). This seasonal variation follows 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/m². The results show that the O₃ concentration is highly correlated to UV irradiance (W/m²) during the daytime (Fig. 17). The diurnal cycles of O₃ and UV radiation are similar, with the O₃ maximum occurring at (16:00 hrs), which is about 2–3 hrs after the UV flux maximum (Fig. 17). Statistical analysis reveals that the correlation between O₃ and UV is significant with a correlation coefficient (R) of 0.82. The annual mean high
radiation was present at around (13:00 hrs) was about 38.8 ±3.5 W/m². The monthly mean maximum and minimum UV radiation were found in May (23.6±2.4 W/m²) and July (16.7±1.9 W/m²) respectively. The most important factors affecting the UV radiation reaching the Earth’s surface are atmospheric ozone, aerosols, solar zenith angle, altitude, cloud cover, atmospheric scattering, and surface albedo. The diurnal variation of NO₂ is maximum during morning and minimum during noon times (14:00-16:00 hrs), owing to higher UV radiation at around (13:00 hrs) (Fig. 17). This leads to higher photolysis rates of NO₂ and results in lower concentrations during these periods. Seasonal mean magnitude of UV and NO₂ was about 23.5±2.4 W/m² and 4 ± 0.4 ppbv in the summer; 18.6±1.9 W/m² and 2.6±0.2 ppbv in the monsoon; 19.3±2.1 W/m² and 3.8 ±0.4 ppbv in the post-monsoon and 19.8±2.2 W/m² and 4.2±0.4 ppbv in the winter, respectively. These investigations elucidate the diurnal variation of NO₂ that has the exactly opposite pattern with the diurnal UV radiation with strong negative correlation coefficient (R= - 0.78), but seasonal variation does not have the inversion relation, suggests, feebly depends on UV radiation. The diurnal variation of CO and SO₂ follows the same pattern, maximum during morning and minimum at noon times (Fig. 17). The major sink of CO is OH radicals besides the anthropogenic activities. The magnitude of OH radical depends on UV radiation through photolysis of ozone. Ozone is a secondary pollutant, which is formed from chemical reactions of its precursors (CO). The higher concentration of ozone and UV radiation leads higher photolysis rates and
results lower concentrations during day time. Hence, the destruction rate of CO moderately depends on the UV radiation. The diurnal variation of CO has the opposite trend with the UV diurnal pattern and shows negative correlation (R= - 0.58). This less negative correlation is mainly due to CO production and destruction does not depend on photolysis rates and also on its sources (natural and anthropogenic activities) over the study region. The diurnal variation of SO\textsubscript{2} has the opposite pattern with the UV variation and shows negative correlation (R= - 0.51), reports UV- A absorption lesser extent to SO\textsubscript{2}.

![Fig.17](image)

Fig.17. The diurnal mean annual variations of SO\textsubscript{2}, NO\textsubscript{2}, CO, O\textsubscript{3}, and UV radiation.

3.12 The effect of SO\textsubscript{2}, NO\textsubscript{2} and CO on visibility

The annual mean diurnal variation of visibility is shown in the Fig. 18. Visibility is a good indicator for the pollution level at any measurement site. It is regarded as a primary index of ambient air quality (Watson et al., 2002).
The loss of visibility is an easily measured symptom of air pollution, arising from a loss of distinction between the object and the background and attenuation of the light signal from the object due to scattering and absorption of light by fine particulates and gaseous pollutants (Sloane and White, 1986). Visibility reduction, meaning we cannot see as far or as clearly through the air. The light absorption caused by carbonaceous particles and scattering is majorly caused by the light scattering of PM$_{2.5}$ (Deng et al., 2008), atmospheric visibility was regressed with PM$_{2.5}$ and Carbonaceous concentrations to study the effect of light impairing components on visibility. 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. Large visibilities appeared from afternoon to evening, while low visibilities occurred in morning. The diurnal variation mainly attributed to anthropogenic emissions, boundary layer processes, chemistry as well as local sources and wind patterns. The higher visibility was present during noon time, owing to the presence of fewer pollutants at the site. Apart from pollutants level exists during this period and boundary layer dynamics also contributes an important role for this enhancement. The low visibility was found at morning, due to high pollutant concentration. The similar diurnal variation of visibility was reported by Xu et al., 2012 and Yunfei Wu et al., 2012. 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).
The results show that visibility significantly depends on the pollutant concentration over measurement location, i.e. high pollution leads to less visibility and low pollution leads to high visibility. The haze is not a natural, caused by anthropogenic air pollution, often carried by the wind. Besides the pollution concentration by anthropogenic activities, high relative humidity can significantly increase the effect of pollution on visibility.

The analysis indicated that the low visibility was primarily caused by the high concentration of PM$_{2.5}$ as a result of the local pollutant accumulation and long-range transport. Consequently, the aerosol particles larger than PM$_{2.5}$ and the water uptake effect of aerosol optical properties could not significantly influence visibility. Sulfate and nitrate were the two most important inorganic aerosol components of PM$_{2.5}$ that obviously decreased visibility. The distribution patterns of sulfate and nitrate concentrations were generally similar to that of PM$_{2.5}$. Generally sulfate and nitrate aerosols are secondary aerosols that are converted from their precursor gases (SO$_2$ and NOx). The presence of higher SO$_2$ and NO$_2$, leads the large extinction coefficient of aerosol components at the measurement site. Carbon monoxide is emitted from the combustion and absorb strongly in the visible, IR due to its graphitic microcrystalline structure. The gas phase chemistry of NO$_2$ is governed by the OH radical chemistry during day time and by the nitrate radical chemistry during night time. NOx is an important contributor to acid deposition, and results formation of secondary organic aerosols from the photo oxidation of isoprene in the presence of NOx (Szmigielski et al., 2010). The life time of
SO$_2$ is low due to reaction with OH and H$_2$O$_2$ in the gaseous and aqueous phase and forms the secondary organic aerosols. Besides, the water vapor content plays key role on visibility, results on degradation of visibility through hygroscopic growth of particles. Oxidants levels are functions of the concentrations of photochemical precursors, i.e. nitrogen oxides (NOx) and sulfur oxides (SOx). Therefore pollution levels are important in determining the rates of oxidation of NO$_2$ to nitrates and SO$_2$ to sulfates. The surface CO, SO$_2$ and NO$_2$ shows the similar diurnal pattern; maximum during the morning and evenings, declined peak is present during noon time. This diurnal variation has the inversion to the diurnal variation of visibility. During the morning period the site was highly influenced by pollutants mainly from biomass burning, solid waste burning and fossil fuel combustion. The emitted scattering and absorption particles strongly degrease the local visibility. The lower SO$_2$, NO$_2$ and CO were found at noon, owing to photo dissociation of NO$_2$ and decreases the anthropogenic activities and higher mixed layer height, results high visibility. After the peak local visibility is gradually decrease to till night, attributed to significant pollutant concentration and OH active reactivity and lower boundary layer height. The negative correlation has been found among SO$_2$ and NO$_2$ with visibility as R= -0.80 and -0.53 respectively (Fig. 19) over the site. It is due to rapid growth of anthropogenic emissions especially fossil fuel consumption and meteorological effects mainly degradation in temperature and mixed layer heights.
These investigations reported that sulfate particles largely reduce the local visibility than nitrates. In humid environments, sulfate particles grow rapidly to a size that is very efficient at scattering light. The similar inversion relation...
was reported by Xu et al., 2012. The diurnal variation of surface ozone has followed the same diurnal variation of visibility, but it does not significantly affect on visibility. In contrast, surface CO has the opposite diurnal pattern with the visibility with strong negative correlation coefficient (R=0.72), due to significant absorption of visible and IR radiation.

### 3.13 Relationships between O₃ and CO

A precise characterization of O₃ and its precursors are useful for the analysis of O₃ chemistry. The annual diurnal mean variations of O₃ concentration are shown in Fig.20. The lower concentrations were found during morning hours (07:00-09:00 hrs) and gradually increased to attain a maximum concentration at around (14:00 hrs), owing to O₃ titration with freshly emitted NO and photochemical formation through the photolysis of NO₂ with high intensity of UV radiation. The low mixing ratios of O₃ observed at night is due to the absence of photo chemical oxidation and titration with NO in the residual boundary layer. The diurnal pattern of CO shows exactly opposite to the diurnal variation of O₃. The result shows that the ozone concentration is high during afternoon hours when the concentration of CO is low. This is mainly attributed to ozone which is photo chemically produced from primary pollutants that are co-emitted with CO. Ozone is formed as a result of photochemical reactions of CO and non-methane hydrocarbons in the presence of sufficient NOx. Ozone is depleted from the atmosphere by reactions with other gas phase compounds, produced OH-
radicals by photolysis (Seinfeld and Pandis, 1998). The lower CO during noon times was caused by high $O_3$, which can produce hydroxyl radical (OH) through the following reactions.

$$O_3 + hv \rightarrow O\ (^1D)$$

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

The major sink of the CO during day time is reaction with OH radicals in the presence of high intensity of UV radiation. Then, CO was converted into $CO_2$ by OH and produces ozone in the following reactions.

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow NO_2 + OH$$  \hspace{1cm} (3.15)$$

The photo dissociation of $NO_2$ produces ozone.

$$NO_2 + hv \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

If NO concentrations are low, however, the following ozone destruction reactions dominate ozone production.

$$OH + O_3 \rightarrow HO_2 + O_2$$  \hspace{1cm} (3.16)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$  \hspace{1cm} (3.17)$$

The correlation between CO and $O_3$ was negative with correlation coefficient ($R= 0.69$) and slope (-0.54) for study period, which indicated that local emission of precursors had significant influence on the formation of ozone. The slope between CO and ozone has been found to be -0.54 suggesting that every 1 ppbv increase in ozone concentration causes a reduction of 0.54 ppbv
surface CO. The less correlation coefficient is due to the different lifetimes of
the two species and complexity of the air masses over measurement site. The
correlation between O₃ and CO can be used as detector of the atmospheric
processes of air masses arriving at a monitoring site.

3.14 Source Identification

3.14.1 SO₂/NOx (RSN)

Air chemistry data can provide valuable information on the sources of
pollutants measured at a site. The relevant chemical species ratios at any site
can help understand air pollution transport between measurement regions to
the surrounding regions. Analysis of chemical species ratio such as SO₂/NOx
indicated that the sites were under the influences of local and regional
emissions to varying extents reflecting the characteristics of emission sources.
surround the respective sites. It is the most important chemical species ratio, to understand the site is impacted by either local or regional contributors and revealed the different characteristics of emission sources impacting on the site. Therefore the values of \(\text{SO}_2/\text{NOx}\) can be used as the fingerprints for distinguishing local air masses from those originating from the rest of the regions. The diurnal variations of RSN for different seasons are shown in the Fig. 21. The diurnal pattern clearly depicts lower RSN values are present during morning period at around (07:00-09:00 hrs) in all the seasons. During the day time higher values are present in all the seasons. 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 are more for monsoon and post monsoon and significant regional contribution for winter and summer. In the diurnal profile the high RSN during noon time suggested that significant regional contribution at site and wind speed also favour for this contribution during these periods. The lower values during the morning hours can be attributed to vehicular exhaustion and sold waste burning over the site. The lower observed ratios in the measurement site can be attributed to the fact that the inventory derived values have considered emissions from both area sources and regional sources; where as mainly affected by low level sources. As discussed above, the high RSN is a characteristic of emission in site. The high \(\text{SO}_2\) to \(\text{NOx}\) considered as the evidence of transport of emissions from other surrounding
regions. The chemical species examinations are suggested that the rural site (measurement site) was characterised by SO$_2$ relative to NOx indicating frequent influences of regional air masses from the other regions.

The ratio of concentrations of SO$_2$ to NOx (RSN) is used to determine the source of pollutant emissions. The RSN is helps in describing source origin contribution on air pollution and generally independent of meteorological conditions (Tasdemir et al., 2005). Gas-phase sulphur dioxide (SO$_2$) is emitted during combustion of all sulfur-containing fuels (coal, oil, and diesel), whereas traffic is a major source of nitrogen oxides (NOx). Sulphur content in emission differs depending on combustion conditions such as electricity generation or transporting this eventually leads to a difference in the ratio of SO$_2$ and NOx. The ratio between the two may be helpful in identifying pollution sources, because fuels used, for electricity generation and transportation differ in their sulfur content and because the ratio is related to combustion conditions. Therefore it is possible to identify the source of pollution from the ratio of SOx and NOx. Air pollution sources are categorized as point, area and line sources based on the emission characteristics. Point sources refer to diplomat huge energy and fuel consumption industrial facilities, such as central heating boilers, power plants and large manufacturers which emit the majority of pollutants. Area sources account for emissions from small industrial factories, and residential activities (Al-Azmi et al., 2009).
The very low values of the S/N ratio (RSN) below 0.48 were associated with high traffic density and the higher than 0.48 suggested the point sources of anthropogenic emission containing high amounts of sulfur (Aneja et al., 2001; Nirel and Dayan, 2001; Goyal and Sidhartha, 2003) over the region. The S/N ratio will change during transport due to different chemical conversions of \( \text{SO}_2 \), \( \text{NO}_x \). The S/N ratio is characterized as (a) very low values (0.12-0.48) are related with traffic, (b) low values (0.43-1.00) are due to the power plant and to daytime emissions of local industry, (c) medium values (0.74-1.90) are associated with local industry emissions and refinery emissions mainly on slow wind episodes, and (d) high values (1.07-4.30) are attributed to refinery emissions during moderate to fast wind episodes.

**Fig. 21.** Seasonal variation of RSN (\( \text{SO}_2/\text{NO}_x \)).

The diurnal mean seasonal pattern clearly depicts lower and higher RSN values are present during morning period at around (07:00-09:00 hrs)
and noon times in all the seasons, suggested mobile source and point source domination respectively, 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 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 (Parrish et al., 1991). The chemical ratio investigations are shows that higher concentration of SO$_2$ to NOx is observed in the case of lower humidity and temperature and lower ratio in wet season attributed to SO$_2$ will be removed by OH reactions in clear sky conditions as well as by wet cloud processes. The investigations were found mobile sources are larger contributors over the site than point sources. A study of the S/N ratio indicates that, in many European countries, the ratio is typically near 1 and is larger than 3 in some countries in central and Eastern Europe, reflecting, the presence of heavy industry. The ratio is generally greater than 1 in industrialized and heavily populated areas of North America, while in areas located away from large stationary sources, it is around 0.1 (Duncan et al., 1995). The S/N ratios in the East Asian source region for different sources were reported for the year 2006, reveals for power, industries, residential and transportation are 1-3, 1-5, 2-5 and less than 1 respectively, While RSN for USA, Germany, Australia, Russia and India are 0.7, 0.9, 0.6, 1.2 and 0.9 (Zhang et al., 2006).

The monthly mean S/N ratio along with surface ozone is depicted in Fig. 22. An interesting feature has been found in this analysis is an obvious
enhancement of \( \text{SO}_2/\text{NOx} \) during the periods of significant \( \text{O}_3 \) peaks. For this analysis we have mainly focus on the influence of local and regional emissions on \( \text{O}_3 \) variation through analysis of chemical species. The diurnal mean monthly maximum S/N ratio was about 0.65 in November and minimum in June about 0.05. The significant enhancement of mixing ratio and decline peaks of \( \text{O}_3 \) were found in November and June about 34 ppbv and 18 ppbv respectively. The diurnal seasonal mean S/N ratio and \( \text{O}_3 \) for monsoon, postmonsoon, winter and summer were about 0.16, 0.32, 0.54, 0.49 and 17, 30, 38, 39 ppbv respectively.

![SO\(_2\)/NO\(_x\) and \( \text{O}_3 \) variation](image)

**Fig. 22.** Monthly variation of RSN and \( \text{O}_3 \)

The chemical species ratio suggested that there is a significant relation between \( \text{O}_3 \) and S/N ratio and the mixing ratio of ozone is strongly depended on regional contribution. It can be seen that elevated levels of ozone observed in the winter and summer were associated with high ratios of \( \text{SO}_2/\text{NOx} \)
suggesting influence of regional emissions from the surrounding regions at the measurement site.

### 3.14.2 Local and regional contribution to OX during winter and summer

The S/N chemical ratio strongly suggested that during the winter and summer significant regional contribution to surface ozone over measurement site. In this study we have used another method (OX-NOx chemistry) to examine the local and regional contribution. The variation in OX concentration with the level of NOx for the winter and summer is presented in Fig. 23 to show the local and regional contributions of OX. The concentration of OX ($O_3$+NO$_2$) is a key indicator of the ability that atmosphere clear pollutants (Jenkin, 2004a) and can be described in terms of the sum of a NOx-independent ‘regional’ contribution ($O_3$ background), and a linearly NOx-dependent ‘local’ contribution (Jenkin, 2004b, Clapp and Jenkin, 2001). The slope (intercept) for OX vs. NOx are 0.48 (30.2) and 0.19(43.4) for winter and summer respectively. Our regional (i.e. NOX-independent) contribution to oxidant is 30.2 and 43.4ppbv for winter and summer respectively. The slope obtained from the regression analysis represented the local OX contribution, while the intercept represents the NOx-independent regional contribution. The NOx-dependent contribution can be considered as a local contribution and correlates with the level of primary pollution. The most important local NOx-dependent contributions are traffic exhaust and oxidant comes from NO reaction with oxygen to form NO$_2$, which is dependent on NO concentration and photolysis rate of radical formation. The studies of combustions-
associated vehicular emissions indicate that the proportion of NO₂ in NOx emissions depends on the type of vehicle, fuel type or driving conditions (Heywood, 1988; Kim et al., 2008; Chen et al., 2009).

Fig. 23. Variation of [OX] with level of [NOₓ] during (a) winter (b) summer.
The positive correlation between NOx and OX provided at measurement site, clear evidence that the local sources substantially contributed in the formation of ozone. Furthermore, it can be seen that the OX at a given location has a NOx-independent contribution and a NOx-dependant contribution. The above analysis also suggested that significant regional contribution was found for ozone formation over the measurement site, especially during winter and summer.

3.14.3 CO to NOx ratio

The ratio of concentrations of CO to NOx is used to determine the source of pollutant emissions. Emission were calculated from the ambient data by plotting the CO-to-NOx mixing ratios and determining the slope (Fujita et al., 1992; Parrish, 2006; Luke et al., 2010). This method is unaffected by pollutants with a significant regional background CO concentration, as the background only affects the intercept of the graph and not the slope. We examined the CO-NOx correlation plots for each season in order to understand the emission ratio of each season. From this ratio analysis, it is possible to determine relative source strengths (mobile vs point sources) by examining the slope of the regression lines, higher slope values are responsible for area sources i.e. vehicle exhaust and lower slopes are associated with point sources, primarily small industries and brick making units and also to determine relative background concentrations by examining the intercept of the regression lines (Saeger, 1989). The slope ($\frac{\Delta [CO]}{\Delta [NOx]}$) and intercept for monsoon, post monsoon, winter, summer were 21.3, 16.5, 8.2, 10.6 and 7.2,
Observations on trace gases

105.1, 254, 61.1 respectively (Fig. 25). The comparatively higher slope values of monsoon and post-monsoon data suggest 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 suggest that significant point sources contribution over the site during these periods. The lower slope value in winter can be attributed to the slower rate of conversion of NOx under lower temperatures. The regional background CO concentrations (intercepts) are elucidated, more was found in post monsoon and winter, decline was found in monsoon.

![Seasonal variation of CO/NOx](image)

**Fig. 24.** Seasonal variation of CO/NOx.

This investigation strongly suggested that local contribution i.e. mobile sources were dominated in monsoon and significant regional contribution (point sources) in winter and summer. On the other hand CO mixing ratios are significantly larger than background values in winter and summer suggest,
local contribution (fossil fuel burning) also plays an important role during these periods.

The diurnal mean seasonal CO to NOx are present in Fig. 24, clearly shows CO to NOx varies from 18 to 95 for all data sets, implied that fossil fuel consumption may contribute more than biomass burning and other oxidation products produced in the measurement area. The much higher CO/NOx (30-95) at the site suggests that very different combustion processes are responsible for the CO observed in winter and summer. The average morning (7:00–10:00) CO to NOx ratios in monsoon (15), winter (27) and summer (34) are higher than those for night time (19:00–22:00) in monsoon (18), winter (39) and summer (54). The ratios of CO to NOx and SO₂ to NOx are supporting the finding that vehicular exhaust emissions play a crucial role on the measurement site.

**Fig. 25.** Correlation between CO and NOx in different seasons.
3.15 Comparison of monthly mean variation of near surface, tropospheric and total ozone

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 NO$_2$ and total ozone. The data corresponding to the grid containing the observation site were used. Total columnar ozone and tropospheric NO$_2$ data are available on daily basis and tropospheric ozone data are available for monthly basis from MLS and OMI. The monthly mean near surface ozone and tropospheric ozone are shown in Fig. 26(a) and 26(b). These two are having similar variations with low values from June through September and increasing trend is observed from December onward, reaching peak observed in summer months (April). The monthly mean variation of tropospheric NO$_2$ exhibits similar to tropospheric ozone (Fig. 26 (c)). Moreover a positive correlation between tropospheric ozone and tropospheric NO$_2$ is clear visible in the scatter plot in Fig. 27 with a correlation coefficient of 0.80. Fig. 26(d) shows a monthly mean variation of total ozone, which is opposite pattern of the tropospheric and surface ozone variations. The monthly mean total ozone increased from March and reached a peak in May, remained high until October and decreased in November Onwards to till February. This variation is mainly due to the strong photochemical activity combined with vertical transport processes characteristics of tropics and is well understood (Staehelin et al., 2001). It has been established that the tropics is a region of intense photochemistry and strong vertical motion of air masses associated
with convective activity (Holton et al., 1995). The vertical motions enable the mixing and transport of trace gases and aerosols from the lower troposphere into the upper troposphere and lower stratosphere (UTLS) region.

![Graphs showing monthly mean values of surface ozone, tropospheric ozone, tropospheric NO$_2$, and total ozone for the study period.](image)

**Fig. 26.** The monthly mean (a) near surface ozone (in ppbv) (b) tropospheric ozone (in DU) (c) tropospheric NO$_2$ (d) total ozone (DU) for the study period.

Recent studies on the climatology of vertical winds at altitudes of 4–22 km at the tropical site of Gadanki (13.5°N, 79.2°E) using the mesosphere-stratosphere-troposphere radar have shown that the months from April to September are characterized by strong vertical winds in the UTLS region.
(Thampi et al., 2009). The reduction in tropospheric ozone, surface ozone, and tropospheric NO₂ during this period (Fig. 26a to 26c) may be partly associated with this strong vertical motion.

![Scattered plot of monthly mean values of tropospheric ozone with tropospheric NO₂.](image)

**Fig. 27.** Scattered plot of monthly mean values of tropospheric ozone with tropospheric NO₂.

### 3.16 Comparative study of Tropospheric O₃

A comparative study has been made by using the MLS and OMI satellite data for the study period from January to December 2012 as shown in the Fig.28. The monthly mean maximum and minimum tropospheric O₃ were observed in May (48 DU) and January (22.8 DU) over Delhi. The enhanced mean value was observed during summer (41 DU) followed by the monsoon (39 DU) and the minimum was observed in the winter (31.3 DU) over Delhi. A maximum mean tropospheric O₃ was observed in summer (41 DU) and in the monsoon (36 DU) and the minimum was observed in the winter (32 DU)
over Pune. For Hyderabad, tropospheric O$_3$ varied from 26-43 DU, with the mean maximum peak noticed during the summer (40 DU) and the minimum during the monsoon (29 DU). Among the measurement locations the high mean concentration was observed over Delhi, with major thermal plants and population density. The regional spread of large point sources such as industries, cement plants and thermal plants are located near Delhi. Low tropospheric O$_3$ was observed in the winter in Delhi and Pune. This is 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.

Fig.28. Seasonal cycle of tropospheric O$_3$ at the different locations in India.
This variation mainly contributes to high population density and associated anthropogenic activities in northern India. This would lead to the formation of several precursors of $O_3$, which is responsible for the photochemical production of $O_3$ with NO$_X$ acting as a catalyst. The tropospheric ozone production mostly depends on photochemical reactions of the precursors (Saraf et al., 2004). Besides the anthropogenic activity, lightning, a major precursor of tropospheric $O_3$, source of tropospheric $O_3$ directly producing NO$_2$. Moreover, it is stronger over northern India compared with the southern region (Christian et al., 2003). From the results it is noticed that, Anantapur has significant tropospheric $O_3$ concentration, which is mainly attributed to the downwind transport of precursors from major pollutant cities.