Chapter 4

Measurements of Particulate Matter and Trace Gases

The urban particulate matter (PM) are mainly fine-mode particles containing a complex mixture of sulfate, soot and smoke (organic and inorganic substances) which have adverse impact on human health (Pope et al., 2000), visibility, regional and global climate (Charlson et al., 1992). An air quality measure of \(\sim 15 \mu \text{gm}^{-3}\) and \(65 \mu \text{gm}^{-3}\) for the annual and 24-hours PM\(_2\) averages has been evolved by the Environmental Protection Agency of USA. In addition, human and industrial activities does lead to copious production of trace gases such as NOx, O\(_3\), CH\(_4\) and aerosols, which are linked through atmospheric chemistry so that emission of a single pollutant can affect several species. The potential impact of trace gases on climate and the correlation among all of the contributing factors is still an outstanding research goal.

Black carbon (BC) aerosol (particulate matter PM\(_1\)), the optically absorbing component of the carbonaceous aerosols has been recognized as the most dominant and main absorbing aerosol causing large radiative heating in the atmosphere. A large concentrations of BC aerosol over south Asia and Indian sub-continent makes this region an extremely climatic sensitive (Lau et al., 2006; Lawrence and Lelieveld, 2010). This Chapter deals with analysis of BC aerosols, PM\(_2\) concentrations and trace gases over Hyderabad and their variations on monthly and seasonal basis. Apart from the local emissions, BC aerosols may be transported thousands of kilometers from their source regions. The concentration weighted trajectory (CWT) technique has been applied for the BC mass concentrations, in order to reveal the source regions that are responsible for the highest BC levels at Hyderabad. The spectral values of the absorption coefficient (\(\sigma_{abs}\)) are also used for the estimation of the Absorption Ångström Exponent (AAE, \(\alpha_{abs}\)), which is an indicator for the BC origin.

4.1 Temporal Variability and Nature of Black Carbon Aerosol over Hyderabad

4.1.1 Temporal Variation of Black Carbon Aerosol Mass Concentration

The BC mass concentrations were measured at TIFR-NBF using Aethalometer on daily basis covering the two-year period (January 2009-December 2010). This section presents the daily, diurnal and seasonal variation of the BC mass fraction over Hyderabad.
Annual and daily variation

The temporal variation of BC mass concentration averaged over six hourly (open circle) and daily mean (filled circle) is shown in Fig. 4.1.1. The vertical bars express the standard error of the mean and the solid horizontal line shows the annual mean BC mass concentration. The data in the Figure reveal a marked daily and annual variation in BC mass concentration. The daily mean BC mass concentration varied from a minimum of 1.06±0.12 µgm\(^{-3}\) during summer to a maximum of 12.50±1.58 µg m\(^{-3}\) during winter exhibiting a mean value of 4.45±0.12 µgm\(^{-3}\). Similar variation in BC mass concentration have also observed over other urban locations in India namely Kanpur (6-20µgm\(^{-3}\) [Tripathi et al., 2005]), Ahmedabad (2-11 µgm\(^{-3}\) [Ramachandran and Kedia 2010]), Pune (4.1 µgm\(^{-3}\) [Safai et al., 2007]) Bangalore (0.4-10.2 µgm\(^{-3}\) [Babu et al., 2002]). Such a large variation in BC mass concentration during winter and summer observed over Hyderabad can not be ascribed to the local contribution alone. Even though the seasonal changes in the boundary layer height may affect the level of BC mass concentration. The strong seasonal variability seen in the data can be associated with the variation in the nature of synoptic wind flow from Northwest to Northeast, which is associated with frequent crop residue and intense biomass burning during winter) and clean marine air from southwest accompanied with rain washout during monsoon.

![Figure 4.1.1: Six hourly (open circle) and daily (filled circle with error bar) variation of BC over Hyderabad during January 2009-December 2010. The horizontal line shows the annual mean value of BC mass concentration.](image-url)
In addition to the annual changes, BC mass concentration also exhibits a pronounced diurnal variation. The monthly average diurnal variation of BC mass concentration is shown in Figure 4.1.2. The individual points at each hour of different days in a month are used to make one hour-average. The figure shows a well defined diurnal variation at Hyderabad with an intense and dominate peak at around 08:00 hours (IST) and the second moderate peak in the late evening around 20:00 hours. The shape and nature of diurnal variation of BC are comparable to the other continental urban and coastal locations in India. The primary and secondary peak in the morning and late evening appears consistently throughout the year but with the varying magnitude. There is a gradual increase in the BC concentration in the morning attains a sharp peak at 08:00 hours. The diurnal variation of BC does show a strong association with the local boundary layer dynamics as well as local anthropogenic activities (Moorthy and Babu, 2002). The primary morning peak can also be associated with the build-up of urban aerosol from anthropogenic activities and fumigation effect in the atmospheric boundary layer which confines aerosols and pollutants from the nocturnal residual layer shortly after the sun rise (Stull, 1998). As the day progresses, the BC mass concentration continuously decreases due to increasing solar heating and reaches the diurnal minima at the local noon hours. The BC mass concentration continue to be lower until 17:00 hours and thereafter it is slowly start to increase and reach a secondary peak at 20:00 hours local time. This increase in the late evening peak is again associated with the shallower nocturnal boundary layer during the night times which leads to rapidly reduction in the ventilation effects and consistently confines the aerosols causing the secondary peak.

Figure 4.1.2: Diurnal variation of BC mass concentration for each month over Hyderabad during January 2009-December 2010.
4.1.2 Black Carbon Aerosols and Boundary Layer Variations

The role of the boundary-layer variations on the BC mass concentration was analyzed. The BC aerosol emissions play an important role in the vertical profiles of the extinction coefficient, while their variability is strongly controlled by the BLH variations. Fig.4.1.3 shows the monthly variation of BLH and BC mass fraction defined as the relative apportionment of BC to the composite aerosol mass concentration, is an index to identify the source contribution of the aerosol particles. Although the contribution of F$_{BC}$ is usually very low but it is an important parameter for the estimation of BC radiative forcing due to its potential radiative effects, which are comparable in magnitude to those of greenhouse gases (Jacobson, 2001). The F$_{BC}$ was calculated from the monthly mean of total aerosol mass and BC mass concentration using the QCM and Aethalometer measurements respectively. The total aerosol mass concentration is not available before July 2009. The BLH was retrieved from the radiosonde measurements considering the BLH as the height where potential temperature presents a sharp gradient.

![Figure 4.1.3: BC mass fraction (histograms) and mixing layer height (line) over Hyderabad during April 2009-March 2010. The vertical bars express one standard deviation from the monthly mean.](image)

The BLH and local emissions are the main factors for controlling the vertical distribution of aerosols (He et al., 2006). During the measuring period BLH showed large monthly variability from ~1.5 km during August-January to ~4 km in April-May (Fig. 4.1.3). This variability is strongly related to air temperature, which can reach upto 37 °C in late pre-monsoon decreasing
further from monsoon to winter. The large convection in pre-monsoon can lift the local emissions into large vertical scale thereby reducing the surface and increases the vertical aerosol concentrations. It is also seen from Fig. 4.1.3, the $F_{BC}$ gradually increases from August to December due to enhanced BC production in winter and the shallower mixing layer, whereas an opposite trend is observed from winter to pre-monsoon due to weakening of BC emissions and deeper boundary layer. These data show that observations $F_{BC}$ varies from 5-15% during the year, while the mean values in winter, pre-monsoon, monsoon and post-monsoon are 13±1.9%, 8.19±2.16%, 7.3±1.8% and 11.8±0.18% respectively. This seasonal variation is similar to the one that was found for the ABL-AOD (Chapter 3.2.3) indicating that the BC aerosols play an important role in the determination of columnar aerosol loading i.e. AOD in the urban environment. This further indicates that the surface extinction coefficients in winter and post-monsoon are contributed mainly due to large BC fraction, whereas in pre-monsoon is due to other aerosols like mineral dust. The observations over Bay of Bengal (BoB) shown that $F_{BC}$ varied from 5.8±0.6% (pre-monsoon) to 2.9±1.15% (post-monsoon) (Sumanth et al., 2004). Simialry, Satheesh et al. (1999) also has reported much lower BC mixing ratio values of 6% over Kaashidhoo in Maldives. The radiative forcing by enhanced presence of elevated layers BC aerosols is known to contribute to regional and global warming, cloud cover and brightness, glacier melting and rainfall redistribution (Menon et al., 2002; Satheesh et al., 2008; Ramachandran and Kedia, 2010), which may play an important role in aerosol forcing efficiency and consequently in atmospheric heating and climate implications over the area mainly during pre-monsoon season.

4.1.3 Potential Source Regions of Black Carbon Aerosol

Concentration weighted trajectory analysis

From a simple air mass back trajectory analysis, it is difficult to extract the information about the relative contribution of the potential source regions of aerosol which contributes at the measurement site. The information can be obtained by quantitative comparison of the transported aerosol determined from the air mass trajectories with the measured aerosol at the site (Seibert et al., 1994, Wang et al., 2006). The Concentration weighted trajectory analysis (CWT) analysis can provide the relative contribution of aerosol from source regions at the receptor site. Using this technique the trajectories reaching the studied location were weighted on the basis of the mean concentration measured at the site during the arrival of the trajectory. Each grid cell in this case is
assigned a concentration obtained by averaging trajectory associated concentrations that had crossed the grid cell:

\[ C_{ij} = \frac{1}{\sum_{k=1}^{M} \tau_{ijk}} \sum_{k=1}^{M} C_{ijkl} \tau_{ijk} \]  

(4.1.1)

Where \( C_{ij} \) is the average weighted concentration in a grid cell \((i,j)\), \( C_l \) is the measured aerosol concentrations at the receptor site, \( \tau_{ijk} \) is the number of \( k^{th} \) trajectory endpoints in the \((i,j)\) grid cell and \( M \) is the total number of trajectory endpoints in \((i,j)\) grid (Seibert et al., 1994). The CWT was applied for the BC mass concentration measured over Hyderabad and result is shown in Fig. 4.1.4. The analysis reveals that the most important potential sources are the IGP, central India and some hot spots in Pakistan territory. It is also seen that contribution from the eastern coast of India is relatively larger than the west coast. Air masses originating from Arabian Peninsula and Persian Gulf traversing the northern AS can also potentially contribute to BC mass concentrations at Hyderabad.

![Figure 4.1.4: Concentration weighted trajectory (CWT) map for BC mass concentration (µg m⁻³) at Hyderabad during January 2009-December 2010. The black circle shows the location of the observation site.](image)
4.1.4 Spectral Variation of Absorption Coefficient

The spectral absorption coefficient ($\sigma_{\text{abs}}$) obtained from Aethalometer measurements at seven wavelengths was used to estimate the Absorption Ångström Exponent (AAE, $\alpha_{\text{abs}}$) using a power law relationship of the form:

$$\sigma_{\text{abs}} (\lambda) = \beta_{\text{abs}} \lambda^{-\alpha_{\text{abs}}} \quad (4.1.2)$$

Where $\alpha_{\text{abs}}$ and $\beta_{\text{abs}}$ are the Ångström and absorption coefficients respectively. The value of $\alpha_{\text{abs}}$ is a measure of spectral dependence of aerosol absorption and is very useful parameter as it contains characteristic features of the sources producing these absorbing particles (Kirchstetter et al., 2004). It is particularly important over India where contribution of BC from biomass/bio-fuel burning is as important as fossil-fuel combustion. The amount of BC from bio-fuel exhibits stronger absorption characteristics compared to fossil fuel BC (Ganguly et al., 2005; Venkataraman et al., 2005). In order to explore the source characteristics of BC aerosols over Hyderabad, the monthly mean values of $\alpha_{\text{abs}}$ were computed using Eq. 4.1.2 and by performing a liner regression of $\ln(\sigma_{\text{abs}})$ vs $\ln(\lambda)$ for the study period January to December 2009. The data is shown in Fig. 4.1.5. It is observed from the figure that the $\alpha_{\text{abs}}$ remained mostly $\sim 1$ during all months over the observation period without exhibiting any strong annual variation; while, slightly lower values are observed for the monsoon season (Jun-Aug). Kirchstetter et al., (2004) have shown that the aerosols produced from the biomass burning exhibits stronger wavelength dependence ($\alpha_{\text{abs}} \geq 2$) in the absorption while those produced from fossil fuel burning such as motor vehicle exhausts etc. show a weaker dependence ($\alpha_{\text{abs}} \leq 1$). The BC aerosols when mixed with dust still have still higher value of $\alpha_{\text{abs}}$ (Kirchstetter et al., 2004). Similarly the atmospheric aerosol mixtures in which absorption is mainly due to BC, exhibit a weak spectral dependence (e.g. Jacobson, 2000; Bond, 2001; Bergstrom et al., 2002). Bond (2001) found that the spectral dependence of light absorption by aerosols is mostly determined by the size of graphite clusters present within the absorbing material, while Bergstrom et al. (2002) reported that stronger absorption at shorter wavelengths could also arise due to the presence of mineral dust in the atmosphere. In view of the above observed weak spectral dependency of absorption coefficient, the results suggest that the BC aerosols observed over Hyderabad mainly originate from fossil-fuel combustion rather than bio-fuel emission. Note that the higher $\alpha_{\text{abs}}$ is indication of higher OC/BC ratio, while low $\alpha_{\text{abs}} \leq 1$ represents high BC/OC,
typical for the fossil-fuel combustion. During monsoon there is larger possibility of increased fraction of non-absorbing aerosols such as sulfate and sea salt which may reduce the $\alpha_{abs}$ values.

![Figure 4.1.5: Monthly variation of absorption Ångström exponent ($\alpha_{abs}$) over Hyderabad during January 2009-December 2010.](image)

### 4.2 Particulate Matter

The concentration of fine aerosols of size $< 2 \mu m$ (PM$_2$) has been recognized as the health standard for clean air. Since these aerosols can enter even in the smallest airway of human body and can generate several respiratory diseases. A comprehensive study of the PM components and its seasonal variation is a key parameter for developing the robust predictive models for urban air quality. The ground-based instruments that can provide the PM measurements directly are highly local. Therefore, large network is required to study the spatial and temporal variability due to complexity of atmospheric physical and chemical processes in different domains. However, several other techniques have been proposed for PM mass concentration using AOD retrievals from polar (van Donkelaar et al., 2010) and geostationary (Paciorek et al., 2008) orbits. The most common technique for PM$_2$ mapping is by obtaining a simple linear regression between columnar AOD measurements from satellites and surface-measured PM$_2$ mass concentration ($\mu g m^{-3}$). The measurements of PM with aerodynamic diameter less than 2$\mu m$ (PM$_2$) using QCM (described in
section 2.2.4) has been carried out over NBF-TIFR campus Hyderabad during the period of July 2009 to May 2010 and the results discussed in the following sections.

4.2.1 Seasonal Diurnal Variation of Particulate Matter and AOD$_{550}$

The diurnal variations of PM$_2$ and MTS-AOD$_{550}$ shown in Fig. 4.2.1 correspond to average pattern in the four typical seasons over Hyderabad. The MTS-AOD$_{550}$ was calculated using Ångström equation (2.2.7) for AOD at wavelengths of 500 and 675 nm. The data clearly show the expected variation where the PM$_2$ concentration is in general high during the morning hours (~9:00) and decreases till 13:00 hrs and then again increases in the evening except for monsoon season. The diurnal pattern of PM$_2$ within Hyderabad urban environment is mainly controlled by the traffic density and boundary layer variations (described in section 4.1.1). The increased traffic density and shallower boundary layer result to the higher PM$_2$ concentrations during the morning hours. It is also seen from the figure that the diurnal variations of MTS-AOD$_{550}$ are in general similar to those of PM$_2$ except for pre-monsoon season mainly attributed to dominance of elevated aerosol layers associated with long-range transport over Hyderabad during these seasons (described in section 3.1.3) and deeper boundary layer (described in section 4.1.2), strong convective eddies and winds. The relationship between surface PM$_2$ and columnar AOD at a place can also vary substantially with the variations in the source regions and aerosol transportation at different altitudes and the presence of multiple structured layers of aerosol at various altitudes having different chemical and physical characteristics. During post monsoon and winter seasons the shallower boundary layer (described in section 4.1.2), frequent temperature inversion, low surface temperature, calm winds, dry and stable atmosphere prevails which inhibits the vertical mixing of aerosol. During the monsoon season the air masses are mixed type originating from southwest and west Asia and well mixed within the shallower boundary layer in majority of the cases which can enhance the association between AOD and PM$_2$. 

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Figure 4.2.1: *Seasonal mean-diurnal variation of AOD$_{550}$ and PM$_2$ over Hyderabad during July2009-May2010.*

### 4.2.2 Intercomparison Study of Satellite and MTS AOD

Satellite observations do provide the aerosol monitoring on a global scale, but have poor temporal resolution and also influenced by cloud masking and surface albedo. Since the remote sensing data can provide AOD values and hence the level of particulate matter as discussed above, an estimate of the air quality using satellite data can be a powerful technique for seasonal monitoring PM$_2$ particularly over urban/industrialized areas. An inter-comparison of MTS-AOD$_{550}$ data was carried out with those measured by MODIS Aqua Terra and MISR derived AODs over Hyderabad. Figure 4.2.2 shows the correlation between the MTS-AOD$_{550}$ with those obtained from MODIS (Terra-Aqua) and MISR over Hyderabad during 2009-2010. The hourly mean MTS-AOD$_{550}$ has been compared for the day of Terra and/or Aqua with ±30 min overpasses following the procedure described by Ichoku et al. (2002). The MODIS (10x10 km) and MISR (17.6x17.6
km) AODs correspond to Level 2 data products. Due to limited observations that satisfy the spatial and temporal selection criteria, one can not draw a definitive conclusion, however, data do show a positive slope on all days with values 0.97, 0.82 and 0.90 and corresponding correlation coefficients between MTS-AOD\textsubscript{550} and MISR, Aqua and Terra and AOD are 0.88, 0.87 and 0.71 respectively. The general agreement between the satellite retrievals and sun photometer measured AODs indicates the potential capability of satellite aerosol monitoring where the ground observations are not available.

![Graph showing correlations between MTS-AOD and MISR, Aqua, and Terra AODs]

Figure 4.2.2: Inter-comparison of Microtops-II AOD and satellite-derived AOD over Hyderabad during July 2009-May 2010.
4.2.3 Estimation of Particulate Matter from Columnar AOD

**PM$_2$-AOD scatter plot**

The scatter plots between collocated measurements of PM$_2$ values and AOD from MTS as well as satellite based Terra-MODIS, Aqua-MODIS and Terra-MISR are shown in Fig. 4.2.3. The results reveal a rather strong correlation between surface PM$_2$ and MODIS-Terra, Aqua and MISR AODs and the correlation coefficients are 0.75, 0.76 and 0.80 respectively suggesting that the satellite remote sensing could be a surrogate and promising technique for the monitoring of surface PM$_2$ on global scale for air quality modeling. The correlation coefficients can be further improved if the surface and vertical profiles of meteorological parameters are incorporated in the estimation of PM$_2$ from the satellite retrievals (Gupta and Christopher, 2009).

![Scatter plots between PM$_2$ and AOD](image)

Figure 4.2.3: Scatter plot between PM$_2$ and AOD obtained from Sunphotometer (a), Terra (b), Aqua (c) and MISR (d) for the ± 30 minute satellite overpass over Hyderabad during July 2009-May 2010.
It is also seen that few points do have large scatter (Fig. 4.2.3). PM$_2$ is the mass concentration of aerosols near the surface whereas the AOD corresponds to the columnar loading. The PM$_2$-AOD correlation could be affected by several factors such as i) the boundary layer variations as day progresses, ii) the wind shear, iii) the vertical mixing caused by instability of the atmosphere, iv) the optical properties and thereby the chemical composition and size distribution of aerosols and iv) the vertical distribution of aerosols. To determine these effects, few representative days were analyzed individually for which large scatter in PM$_2$ vs AOD plot is seen using vertical profiles of extinction coefficient obtained from night time micro pulse lidar measurements (described section 2.2.6) for the corresponding day along with meteorological parameters. The meteorological parameters were taken from the University of Wyoming data base record for Hyderabad station, which is 15 km away from the observation site. Figure 4.2.4(a-c) shows the scatter plot between PM$_2$ and MTS-AOD$_{550}$ (left panel) and the vertical profiles of the extinction coefficient along with meteorological parameters (right panel) for three particular days and the results are discussed below:

**September 10, 2009**

The lidar measurements of extinction coefficient on September 10, 2009 (Fig. 4.2.4a) reveals the presence of elevated aerosol layers with two prominent peaks at ~0.2 km and ~ 2 km extending upto ~4 km. The potential temperature (θ) profile clearly shows a well-mixed layer up to 1 km which is accompanied with high wind speed (>10m/s). Since the September month is part of Indian summer monsoon during which convective eddies (vertical aerosol transport mechanism) are not so strong and the vertical transport of aerosols will take place only by vertical shear of horizontal wind as supported by the strong winds >12ms$^{-1}$ at 1km. In addition, the higher elevated aerosol layers (above 1km) could also be due to long-range transport associated with south-westerly winds which is more prominent in this region during monsoon season. The chemical components of atmospheric aerosols over Hyderabad was simulated using OPAC model (section 6.2) show that water soluble and sea-salt dominate during the monsoon season which substantially enhances the columnar AOD despite their lower concentrations at the surface. Therefore the negative correlation between PM$_2$ and AOD$_{550}$ can be ascribed to elevated aerosol layers and dominance of scattering type coarse-mode particles.
**4 November 2009**

The extinction coefficient profiles on November 4, 2009 (Fig. 4.2.4b) also shows the distinct aerosol layers above few meters from the surface. During this period extensive forest fires occur in Southeast Asia that transport over Hyderabad by the northeasterly winds. The transport of biomass-burning aerosols can lead to the enhanced extinction coefficient extended upto ~3.5 km. The steady variation of vertical profile of potential temperature (θ) from the ground to ~2 km suggests the convectively stable and well-mixed atmospheric layers coupled with a strong inversion at 2 km and 2.6 km and a stable atmospheric layer afterwards. The inversion in θ correspond to the drastic change in wind direction from northeast to southwest at 2 km indicating the advection of aerosol mass of different origin (*section 3.2.4*). The vertical profile of RH shows a steady increase from surface to ~3.5 km can cause the particles growth and enhances the extinction coefficient. Despite the shallower boundary layer the elevated aerosol layers from long-range transport from the various sources can substantially reduce the correlation coefficient of AOD-PM$_2$.

**11 March 2010**

March is a pre-monsoon month over the study region. During this month very high aerosol extinction coefficient are observed near the surface which decrease drastically upto 0.5 km (Fig. 4.2.4c). The excess aerosols can be associated with the increase in secondary aerosol formation at the surface due to increase in temperature and solar radiation. The vertical profile of potential temperature shows an unstable atmosphere from 1 km to ~3.5km. Drastic changes in RH, wind speed and direction are also observed which strongly modify the vertical mixing of aerosols. The vertical wind shear and convective instability conditions are stronger in the pre-monsoon season due to high surface temperature in Hyderabad which also enhances the vertical mixing. The aerosols over Hyderabad during pre-monsoon season are a mix of water soluble, insoluble, dust and sea-salt particles and therefore significantly increase the columnar AOD. The RH ranges from 29 to 79 % bellow 1 km and it decreases from 65-8 % above 3 km also confirming the presence of absorbing type dust layers. Since the PM$_2$ defined as the mass concentration of fine-mode particles while AOD represents the columnar aerosol loading contributed from both fine and coarse-mode particles, a correlation between PM$_2$ and AOD is week during pre-monsoon season, when the coarse-mode particles (dust, sea-salt) are dominated.
In summary, the present analysis demonstrates that the surface aerosol measurements cannot be fully representative of the columnar ones, since the monitoring of PM from columnar measurement is based on the assumption that aerosols are well mixed within the boundary layer. However, this assumption is not applicable for the several cases when elevated aerosol layers of various chemical composition and size (fine and coarse) occur above the boundary layer due to the instability of the atmosphere and long-range transport.
Estimation of Particulate matter

The estimation of concentration of surface PM$_2$ from the columnar AOD measurements is given by an empirical relation:

\[ \text{PM}_2 \, (\mu g m^{-3}) = m \times \text{AOD} + C \quad (4.2.1) \]

Figure 4.2.4 (a-d) shows that time-series of the measured hourly-averaged PM$_2$ within ±30 min of satellite overpass and the calculated PM$_2$ from MTS, Terra, Aqua and MISR AOD using the linear equation 4.2.1 and slope values shown in Fig 4.2.3. As it can be seen the measured daily PM$_2$ values shows close agreement with the satellite calculated values. However, some deviations of calculated PM$_2$ from the measured values during pre-monsoon and in some cases in the monsoon season (described in section 4.2.1 and 4.2.3) are also observed. For several cases the calculated PM$_2$ values from MT and Terra are higher as compared to measured values and this is more prominent in pre-monsoon season with values ranging from 2.52-16.98 µgm$^{-3}$ and 3.25-12.5 µgm$^{-3}$ with mean difference of 6.19±0.41 µgm$^{-3}$ and 8.07±3.09 µgm$^{-3}$ for MTS and Terra, respectively, which are well within the measurement uncertainty of the ground based instrument (described in section 2.2.4). In contrast, the calculated PM$_2$ values from Aqua-MODIS and MISR are higher as compared to measured ones and the mean difference was found to be 7.12µgm$^{-3}$ and 3.03 µgm$^{-3}$ respectively. These results have important implications for the satellite monitoring of PM.
particularly over the regions where ground based monitoring is sparse. The monitoring of PM$_2$ from AOD measurement relies on the assumption that AOD and PM$_2$ are linearly related to each other. However, the AOD-PM$_2$ relationship varies significantly in space and time with changes in aerosol type and size, vertical heterogeneity and quality of AOD retrievals. A simple AOD-PM$_2$ relationship has potential to estimate PM$_2$ at surface but does not provide a great accuracy. The majority of the satellite aerosol retrieval algorithms assume the dark-target approach to obtain AOD values; therefore, retrievals over bright surfaces (such as desert and bright urban areas) are not up to the mark. Other satellite sensors such as MISR, which can derive AOD even over bright targets using multi-angle measurements, may be more suitable for such estimations. Knowing the uncertainties in satellite data over bright targets, PM$_2$ estimation from space remains a real challenge in the urban regions over the globe.

Figure 4.2.3: The time-series of collocated hourly average of measured and calculated PM$_2$ within ±30 minutes of satellite overpass and their differences (black horizontal line). The Sun photometer AOD are collocated with PM$_2$ with respect to Terra overpass over.
4.3 Measurements of Trace Gases over Hyderabad

Despite relatively small mass, the Earth’s biosphere plays a major and increasing role in changing the Earth’s climate. The human activities have caused several phenomena such as ozone hole, acid rain, deterioration of urban and regional air pollution, climate change, etc. attributed mainly to the increasing emissions of various gaseous and particulate species. Recognizing the impacts of human activities on the environment and climate, particularly changes in composition and chemistry of the atmosphere on local, regional and global scales, scientific attentions have been attracted over the past several decades. In addition to these, human activities have also directly affected the terrestrial life. Among many topics, the potential impact of trace gases on climate and related factors have received outstanding research activities.

The adverse consequences of increased industrial activity and the general economic prosperity are the emission of large amount of black carbon, trace gases and various precursor gases over Hyderabad. Chemical transformations of these primary pollutants in the presence of UV solar radiation lead to secondary pollutants that are major health and environmental concerns. For example, the atmospheric ozone plays an important role in the photochemical processes in the troposphere but it also has strong oxidant properties, which at certain ambient concentration levels may cause damages to humans, animals and vegetation (Finlayson-Pitts and Pitts, 1997; Bates, 1994).

The measurements of trace gases (\(O_3\), CO, NOx and \(SO_2\)) along with meteorological parameters have been carried out at TIFR-NBF, Hyderabad campus during January – December, 2010. Mixing layer height (MLH) is derived from the radiosonde measurements for the study period. The seasonal variations of these gases have been studies in view of local emissions, planetary boundary layer (PBL) variations.

The monthly mean variation of meteorological parameters during Jan-Dec 2010 is shown in Fig 4.3.1 and summarized in Table 4.3.1. As expected, all the parameters (except for wind speed) showed the marked seasonal variability. More specifically, the ambient surface temperature, RH and mixing layer height vary from 22 - 31, 47 - 74 % and 2.2 to 4.5 km and their respective highest values are (31.22±1.73), (74.02±9.42) and (4.54±0.48) during the pre-monsoon, monsoon and pre-monsoon respectively. The boundary layer becomes deeper during pre-monsoon season because of the intense solar flux (Fig.4.3.1 and Table 4.3.1) and resulting strong turbulent eddies
which in turn distribute the pollutants in a greater volume of the troposphere and causing their lower surface concentrations. During post monsoon and winter season, mostly calm north easterly winds prevailed (<3ms\(^{-1}\)) and relative humidity also decreased substantially indicates that the north easterly winds carry dry and polluted air from north India and South East Asia. The seasonal mean value and standard deviation of meteorological parameter along with measured trace gases is summarized in Table 4.3.1.

Table 4.3.1: Seasonal mean value of meteorological parameters and trace gases measured at Hyderabad during January-December 2010.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Winter</th>
<th>Pre-Monsoon</th>
<th>Monsoon</th>
<th>Post Monsoon</th>
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<tbody>
<tr>
<td>(T(\degree C))</td>
<td>22.11±2.25</td>
<td>31.22±1.73</td>
<td>26.54±2.02</td>
<td>22.95±3.39</td>
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<tr>
<td>RH(%)</td>
<td>56.28±0.21</td>
<td>47.18±6.84</td>
<td>74.02±9.42</td>
<td>70.71±0.08</td>
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<tr>
<td>Sol Rad (Wm(^{-2}))</td>
<td>519.97±54.72</td>
<td>596.00±18.55</td>
<td>450.87±54.99</td>
<td>475.83±58.57</td>
</tr>
<tr>
<td>WS (ms(^{-1}))</td>
<td>2.34±0.35</td>
<td>3.46±1.17</td>
<td>3.14±1.61</td>
<td>2.73±0.20</td>
</tr>
<tr>
<td>WD (deg)</td>
<td>121.99±7.60</td>
<td>188.33±22.03</td>
<td>220.31±26.47</td>
<td>138.85±23.03</td>
</tr>
<tr>
<td>MLH (km)</td>
<td>2.54±0.41</td>
<td>4.54±0.48</td>
<td>2.81±0.44</td>
<td>2.26±0.09</td>
</tr>
<tr>
<td>(O_3) (ppbv)</td>
<td>31.29±3.70</td>
<td>39.37±1.60</td>
<td>18.24±5.45</td>
<td>23.33±5.89</td>
</tr>
<tr>
<td>NOx (ppbv)</td>
<td>9.14±1.40</td>
<td>5.33±0.87</td>
<td>3.07±0.32</td>
<td>6.43±2.15</td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>171.90±21.85</td>
<td>254.45±56.17</td>
<td>98.00±30.09</td>
<td>103.11±10.4</td>
</tr>
<tr>
<td>(SO_2) (ppbv)</td>
<td>17.39±3.22</td>
<td>10.07±2.45</td>
<td>5.75±1.23</td>
<td>9.13±0.10</td>
</tr>
</tbody>
</table>

Figure 4.3.1: Monthly variation of meteorological variables over Hyderabad during January-December 2010.
4.3.1 Ozone

The tropospheric ozone \((O_3)\) is a trace gas that plays a controlling role in the oxidation capacity of the atmosphere through the formation of OH radical. Ozone and its photochemical derivative OH are the major oxidants for most of the reduced trace gases in the troposphere. Without \(O_3\), reduced gases such as CO, hydrocarbons and most of the sulfur and reactive nitrogen compounds would accumulate to the levels substantially above those in the present atmosphere. Environmentally, higher level of \(O_3\) concentrations at the surface is a major pollutant because of their detrimental effects on human health and plants. Elevated levels of \(O_3\) have been observed in the regions of industrialized as well as developing countries. Tropospheric ozone also plays an important role in the radiative balance. It dominates in several important environmental problems such as, impact on air quality as an oxidizing pollutant that is harmful to biosphere and agricultural crop production. Chameides et al., (1999) concluded that enhanced ozone concentration over China substantially reduces the crop yield of winter wheat. Similarly, tropospheric ozone is a secondary pollutant and it is produced by several mechanisms in the troposphere, which are mainly controlled by the meteorological conditions, long-range transport and geographical location.

The annual variation (from monthly mean data) of surface ozone mixing ratio at Hyderabad is shown in Fig. 4.3.2. The mixing ratio of \(O_3\) shows higher values during the pre-monsoon (39.37±1.60) and winter (31.29±3.70) ppbv seasons. The higher level of \(O_3\) concentration during pre-monsoon (March-May) can be attributed to the enhanced photochemical reaction caused by the increasing solar radiation (Fig.4.3.1). A comparison of the annual variations of surface ozone for five urban sites in India is given in Table 4.3.2. Eventhough due to the different sampling periods, it is difficult to arrive at a definitive conclusion, the pronounced seasonal variation in surface ozone is clearly seen individually in each data set. Interestingly, the seasonal variations of \(O_3\) observed over Hyderabad are different from Ahmedabad and Pune but similar to observed over Delhi in spite of their almost similar annual mean values (Table 4.3.2). Yamaji et al. (2006) showed that the \(O_3\) concentration over East Asia is strongly influenced by the chemical production of regional emissions during summer season. However, the high concentration during winter (Dec-Feb) could be due to the inflow from the north and north-eastern regions especially from the IGP carrying rich polluted air combined with the shallower boundary layer, stagnant air masses and weakening of wet deposition due to lack of adequate precipitation (Fig. 2.1.1). The lower mixing
ratio of surface O$_3$ during the monsoon season could be associated with the (i) inadequate sunshine inhibiting the photochemical production of O$_3$ less effective, ii) changes in the synoptic wind from moderately low northeasterly to strong southwesterly that carry less polluted and moist air transported from the marine atmosphere (Fig. 2.1.1) and iii) rain washout of the pollutants. Pochanart et al. (1999) estimated the regional scale photochemical buildup of O$_3$ from anthropogenic contribution in northeast Asia (Oki island) using back-trajectory analysis during March 1994 to March 1996. The results showed that the photochemical O$_3$ caused by anthropogenic activities in this region was estimated to be 21 ppbv in summer and very less (3 ppbv) in winter. Surface measurements of O$_3$ climatology have been reported for a wide range of latitudinal coverage by Tanimoto et al. (2005), who concluded that the latitudinal dependence of the seasonal cycles particularly the amplitude and phase of the O$_3$ spring maximum, were significantly modulated by transport mechanisms and strength of Asian continental outflow. The concentration of O$_3$ from east China to Japan at around 35-40$^\circ$N was found to be 55-60 ppbv in March-April and 55-65 ppbv in May-June (Yamaji et al., 2006) which are slightly higher than the present study. Wild et al. (2004) reported that the contribution from the industrial and fossil fuel sources to the O$_3$ production in Europe and North America were 0.5-3.5 ppbv and 1.0-3.1 ppbv, respectively. The seasonal variation of mixing ratio of surface O$_3$ are well correlated with its precursor gases such as CO and NOx (Fig.4.3.2). The production of O$_3$ in the troposphere is mainly controlled by the oxidation of CH$_4$, CO and hydrocarbons in the presence of NOx (Crutzen, 1974).

Table 4.3.2: Monthly mean variation of Surface Ozone (ppbv) at Delhi, Ahmedabad, Pune and Hyderabad.

<table>
<thead>
<tr>
<th>Months</th>
<th>Delhi O$_3$</th>
<th>Ahmedabad$^a$ O$_3$</th>
<th>Ahmedabad$^a$ NOx</th>
<th>Pune$^b$ O$_3$</th>
<th>Pune$^b$ NOx</th>
<th>Hyderabad O$_3$</th>
<th>Hyderabad NOx</th>
<th>Trivandrum$^b$ O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>17.0</td>
<td>38.4</td>
<td>10.1</td>
<td>37.6</td>
<td>16.1</td>
<td>28.11</td>
<td>8.95</td>
<td>20.0</td>
</tr>
<tr>
<td>February</td>
<td>22.7</td>
<td>43.2</td>
<td>10.6</td>
<td>54.6</td>
<td>13.5</td>
<td>30.41</td>
<td>7.85</td>
<td>19.7</td>
</tr>
<tr>
<td>March</td>
<td>29.7</td>
<td>40.8</td>
<td>11.4</td>
<td>52.5</td>
<td>11.2</td>
<td>41.21</td>
<td>6.33</td>
<td>16.1</td>
</tr>
<tr>
<td>April</td>
<td>34.0</td>
<td>25.5</td>
<td>8.6</td>
<td>42.5</td>
<td>8.5</td>
<td>38.59</td>
<td>4.90</td>
<td>14.0</td>
</tr>
<tr>
<td>May</td>
<td>37.0</td>
<td>16.0</td>
<td>5.1</td>
<td>27.5</td>
<td>6.8</td>
<td>38.32</td>
<td>4.77</td>
<td>12.1</td>
</tr>
<tr>
<td>June</td>
<td>27.4</td>
<td>13.2</td>
<td>-</td>
<td>20.4</td>
<td>3.6</td>
<td>25.29</td>
<td>3.51</td>
<td>9.0</td>
</tr>
<tr>
<td>July</td>
<td>17.7</td>
<td>16.8</td>
<td>-</td>
<td>17.5</td>
<td>2.8</td>
<td>19.69</td>
<td>3.10</td>
<td>7.7</td>
</tr>
<tr>
<td>August</td>
<td>15.4</td>
<td>19.0</td>
<td>-</td>
<td>12.2</td>
<td>3.2</td>
<td>14.68</td>
<td>2.76</td>
<td>7.5</td>
</tr>
<tr>
<td>Month</td>
<td>17.5</td>
<td>17.9</td>
<td>7.1</td>
<td>14.9</td>
<td>4.1</td>
<td>13.27</td>
<td>2.92</td>
<td>7.6</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>------</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
<td>-------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>September</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>October</td>
<td>24.6</td>
<td>26.0</td>
<td>8.0</td>
<td>25.0</td>
<td>8.6</td>
<td>27.49</td>
<td>4.91</td>
<td>10.0</td>
</tr>
<tr>
<td>November</td>
<td>23.2</td>
<td>30.5</td>
<td>10.3</td>
<td>32.5</td>
<td>15.5</td>
<td>19.17</td>
<td>7.95</td>
<td>12.3</td>
</tr>
<tr>
<td>December</td>
<td>20.0</td>
<td>28.0</td>
<td>14.4</td>
<td>34.0</td>
<td>20.7</td>
<td>35.34</td>
<td>10.63</td>
<td>14.1</td>
</tr>
<tr>
<td>Annual</td>
<td>23.85</td>
<td>26.27</td>
<td>9.51</td>
<td>30.93</td>
<td>9.55</td>
<td>27.63</td>
<td>5.71</td>
<td>12.51</td>
</tr>
<tr>
<td>mean</td>
<td>(6.98)</td>
<td>(10.25)</td>
<td>(2.69)</td>
<td>(14.02)</td>
<td>(5.89)</td>
<td>(9.53)</td>
<td>(2.61)</td>
<td>(4.44)</td>
</tr>
</tbody>
</table>

\[ a= \text{Lal} \ (2007) \]
\[ b= \text{Beig et al.} \ (2007) \]

Figure 4.3.2: Monthly variation of the trace gases concentration over Hyderabad during January-December 2010. The vertical bars express one standard deviation from the monthly mean.

### 4.3.2 Nitrogen oxides

The oxides of nitrogen (NOx = NO+NO2) are produced by both natural (mainly lightning and microbiological processes in soil) and anthropogenic sources (fossil fuel combustion and biomass burning; (Table 4.3.3) and play an important role in tropospheric Ozone chemistry, hydroxyl radical formation (oxidation) and secondary aerosol formation, etc. The photolysis of NOx in the troposphere leads to the formation of O3. The regional distribution is strongly controlled by the
local emissions, while in the midtroposphere and upper troposphere it is mainly associated with the long range transport (Kunhikrishnan et al., 2006). Long term air quality monitoring over the residential and industrial locations in Indian cities indicates the NOx concentration have been increasing at alarming rate and at some locations it has already exceeded the permissible limits as high as 100 to 240 µgm⁻³ and expected to increase in upcoming years (Kunhikrishnan et al., 2006). It is recognized as one of the most important key parameter for the study of air quality as well as the radiation budget and it represents the 10-15% of the total radiative forcing of the anthropogenic green house gases in the atmosphere (Wild et al., 2001).

High concentrations of NOx are harmful to vegetation and human health. The annual variation of NOx mixing ratio over Hyderabad is shown in Fig 4.3.2. The result shows the marked seasonal variability in NOx mixing ratio with higher concentrations during winter (9.14±1.40) and lower concentration during the monsoon (3.07±0.32). Similar to the present study, the high value in winter and lower value in monsoon season are reported from the satellite as well as ground based observations over Pune [18.53°N,73.80°E] (Ghude et al.,2008) and Trivandrum [8.53°N, 76.87°E] (David and Nair, 2011). The annual mean and median values of NOx are 5.71 ± 2.61 ppbv and 4.91 ppbv, respectively. The almost similar values for both mean and median suggests the homogeneous sources of NOx at Hyderabad. However, the seasonal variability in NOx mixing ratio is strongly correlated with the regional emissions as well as long range transport from polluted sites such as IGP, south East Asia (mainly China) accompanied with intense biomass burning in these regions during winter. Kunhikrishnan et al., (2006) reported that 15-25% of NOx in the middle troposphere (850-500 hPa) to upper troposphere (500-150 hPa) regions over India is sensitive to emissions from the Africa, Southeast Asia and China. Authors also reported that 20-30% of boundary layer (surface to 850hPa) O₃ over India is sensitive to local NOx emissions and almost irrespective of the seasons.

4.3.3 Carbon Monoxide

Carbon Monoxide (CO) plays an important role in atmospheric chemistry and acts as an indirect greenhouse gas. CO is produced by natural as well as anthropogenic sources such as oxidation of volatile organic compounds (VOCs), methane and non-methane hydrocarbon (NMHC), biological processes and incomplete combustion of fossil fuels and biomass burning (Table 4.3.3). Since it is mainly produced by anthropogenic activity, the CO concentration in the Northern hemisphere is
much higher (~150PPB) as compared to the Southern hemisphere (~50 ppbv). Due to variety of sources and short atmospheric lifetime (~1-3 months), CO concentration shows large gradient and its global burden of about 360 Tg is highly uncertain compared to those of the CH$_4$ and N$_2$O (IPCC, 2001). The results from the globally distributed network indicates that CO decreased globally by about 2%/yr from 1991 to 1997 (Novelli, 1998) and increased in 1998 (IPCC, 2001).

The annual variation CO mixing ratio over Hyderabad is shown in Fig. 4.3.2. The result shows the strong dependency of the CO mixing ratio on the meteorological conditions and the variation in the boundary layer. The variations in boundary layer (Fig 4.3.1) play an important role in the seasonal changes in mixing ratio. However, the mixing ratio of CO is higher in pre-monsoon (254.45±56.17ppbv) despite the deeper boundary layer (Fig.4.3.1) and lower (98.00±30.09 ppbv) during monsoon season. The higher concentration of CO during pre-monsoon season could be associated with the biomass as well as crop residue burning (described in section 3.1.1). The lower and stable value during monsoon could be ascribed by the mixing of clean marine air masses with the continental one within the boundary layer and relatively calm wind <4 ms$^{-1}$ (except for August). It is interesting to note that the seasonal variation of CO over Hyderabad is different from Ahmedabad and later shows the higher concentration during winter season (Sahu and Lal, 2006). The seasonal variability in mixing ratio of CO over Hyderabad could also be associated with the abundance of OH in the atmosphere (Novelli et al.2003). The atmospheric OH is main oxidizing agent in the troposphere and the major sink for CO. The atmospheric abundance of CO also affects the tropospheric O$_3$, depending on the NOx concentration (Crutzen et al., 1985).

In general, BC is known to be well correlated with CO due to their co-emission from the incomplete combustion of fossil and biomass fuels. However, the emission ratio of BC/CO (E$_{BC}$/E$_{CO}$) may depend on the emission sector, even if they can be co-located [Bond et al., 2004, Sahu et al., 2011]. Ideally, in ambient air, the correlation between BC and CO depends on the several factors such as i) wet and dry deposition, ii) vertical mixing and convection, iii) long range transport, iv) reaction of CO with OH radical and v) secondary emissions of CO through the oxidation of anthropogenic and biogenic VOCs and methane [Hudman et al.,2008]. Scatter plots using hourly averages of BC mass concentration and CO mixing ratio from the present measurements is shown in Fig 4.3.3. The data plotted for four different seasons at Hyderabad during January-December 2010 reveal the positive correlation, strong variability in slope (BC/CO
ratio) and intercept values for all seasons. The seasonal variability in BC/CO ratio can be attributed to emissions from different sources and transport paths. Assuming the negligible role of scavenging of BC due to precipitation, the BC/CO ratio can be used as surrogate distinguishing different pollutant sources in mixed urban plume. However, the emissions of these species are mostly from mobile sources in Hyderabad. Therefore, lower BC/CO ratio can be expected compared to the air masses influenced by the emissions from industry, chemical manufacturing plants and truck traffic (Spackman et al., 2008). The correlation coefficient of BC-CO was found to be higher during post monsoon (0.86) and pre-monsoon (0.79) attributed to the intense biomass and crop residue burning. The lower correlation of BC-CO during winter could be due to wet deposition caused by moist air masses carrying by northeasterly wind from IGP (section 3.1.3). More interestingly, the non-linearity in the BC-CO correlation at the CO intercept during pre-monsoon seasons is most likely related to the time scales for BC removal that are significantly shorter than those for CO photochemical loss. As BC particle ages, it undergoes a transformation from hydrophobic to hydrophilic by forming an internal mixture with water soluble aerosol such as sulfate and organic components which enhances the BC removal by wet deposition and sedimentation (Spackman et al., 2008). It is also supported with the OPAC simulation (described in section 6.2) indicating the dominancy of water soluble aerosol component (Table 6.2.1) during pre-monsoon season. Dickerson et al. (2002) also reported the similar results regarding BC-CO relationship and they found that correlation coefficient and slope value over Indian ocean, Kaashidhoo (KCO) are (0.74 and 0.0125 gBC/gCO), (0.81 and 0.015 gBC/gCO) respectively during INODEX. However, this comparison could be treated as qualitative rather a quantitative due to spatial variability in source fuel type, secondary sources of CO from VOC oxidation and atmospheric processes (e.g. mixing, transport, wet deposition).
4.3.4 Sulfur dioxide

Sulfur dioxide (SO₂) enters into the atmosphere as a result of both natural phenomena and anthropogenic activities, such as fossil-fuel combustion (Table 4.3.3), oxidation of organic materials in soils, volcanic eruptions and biomass burning and is oxidized quickly in the atmosphere, leading to aerosol formation and acid deposition (IPCC, 2007). The oxidation of SO₂ via gaseous phase reaction with OH is an important source of sulphate aerosol in the atmosphere (Penner et al., 2001). The estimated global emissions of SO₂ range from 66.8 –92.4 TgSyr⁻¹ for anthropogenic emissions in the 1990s and 91.7-125.5 TgSyr⁻¹ for total emissions (IPCC 2007). However, the emissions growth of SO₂ in India during 1996-2010 was found to be 70% (Lu et al., 2011). The changes in the abundance of SO₂ have an impact on atmospheric chemistry as well as the Earth’s radiation budget and consequently the climate system. The seasonal variation of the SO₂ lifetime inferred over the eastern United States from in-situ measurements and the GEOS-Chem simulations indicates that the SO₂ lifetime in winter is about three times as long as it is in summer (Lee et al., 2011).

Fig. 4.3.2 shows the annual variation of mixing ratio of surface SO₂ over Hyderabad during January-December 2010. The result shows higher values during the winter (17.39±3.22) ppbv and
lower during monsoon (5.75±1.23) ppbv and their annual mean and median values are (10.3 ± 4.98) ppbv and 9.13 ppbv, respectively. Sharma et al., (2009) reported the seasonal variation of SO₂ during 2008 over Delhi. The seasonal mean values of SO₂ over Delhi is different [1.97±0.85 (winter), 1.01±0.48 (summer) and 1.15±0.04 (autumn)] and found to be very low as compared to present study. The low values of SO₂ over Delhi could be due to limited days of sampling (~20 days for a particular month of each season) which can not be the representative for any season. The higher concentration of SO₂ over Hyderabad is attributed to location of the measurement site, which is surrounded by the several chemical and parametrical industries along with the petroleum storage facilities. It is also noticed that the seasonal variation indicates that the mixing ratio of SO₂ is mainly controlled by the nature of air mass and meteorological conditions. More specifically, the declination of SO₂ during monsoon with enhanced humidity could be associated with the cloud processes (Igarashi et al., 2006). Carmichael et al., (2003) reported that the annual median SO₂ concentration measured in equatorial and northern Africa is 0.1ppb which is substantially lower as compared to the present study.

The concurrent measurements of CO, NOx and SO₂ can help characterize the sources of emissions. The mobile source are characterized by high CO/NOx and low SO₂/NOx ratio, while the point sources correspond to high SO₂/NOx and low CO/NOx ratio. The annual mean value of CO/NOx and SO₂/NOx ratio were found to be 29.67 and 1.84 respectively, suggesting that enhanced concentrations of CO, NOx at Hyderabad are mainly contributed by the mobile sources. The CO/NOx and SO₂/NOx ratio were found to be 50 and 0.6 over Delhi (Aneja et al., 2001), indicates that the more mobile and lesser point sources as compared to Hyderabad.

Table 4.3.3: Contribution of various sources for precursor gases in India (adopted from Lal 2007).

<table>
<thead>
<tr>
<th>Sectors</th>
<th>NOx (%)</th>
<th>SO₂ (%)</th>
<th>Sources</th>
<th>CO(Tgyr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Generation</td>
<td>27.9</td>
<td>46.1</td>
<td>Bio-fuel</td>
<td>34.2</td>
</tr>
<tr>
<td>Transport</td>
<td>32.0</td>
<td>7.8</td>
<td>Coal sector</td>
<td>16.8</td>
</tr>
<tr>
<td>Industry</td>
<td>19.2</td>
<td>34.4</td>
<td>Crop residues</td>
<td>12.0</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>18.7</td>
<td>5.2</td>
<td>Fossil fuel</td>
<td>6.3</td>
</tr>
<tr>
<td>Other sectors</td>
<td>1.9</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-energy sources</td>
<td>0.3</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.4 Radiative Impact of Trace Gases

Radiative forcing is an externally imposed change in the radiative energy budget of the Earth’s climate system and it is contributed by several factors such as variations in solar insolation, alteration in surface boundary conditions related to land-use change and desertification, or natural and anthropogenic perturbations to the radiatively active species such as aerosols and trace gases in the atmosphere (IPCC 2001, Collins et al., 2006). Without the green house gases, the Earth’s surface temperature would have been much bellow than what it is today (i.e. -18$^\circ$C to +14$^\circ$C). Detailed descriptions of the radiative forcing due to aerosols are presented in Chapter 6. The trace gases namely Ozone and water vapour were also included in the estimation of aerosol radiative forcing. A current scientific evaluation on the radiative forcing due to green house gases is provided for the sake of completeness.

The green house are an important absorbing agent of the Earth’s atmosphere; for example, UV radiation is absorbed by the stratospheric ozone while the outgoing thermal radiation is absorbed by other trace gases (e.g. CO$_2$, H$_2$O) in the NIR; these processes perturbed the Earth’s radiation budget so called the radiative forcing in turn increases the surface temperature of the Earth so called green house effect. However, it should be noted that the radiative forcing due to changes in the concentration of a single forcing agent can be strongly affected by emissions of several compounds (IPCC, 2007), e.g. the radiative forcing of CH$_4$ is affected by CH$_4$ as well as NOx emissions (IPCC, 2007).

The well-mixed greenhouse gases have lifetimes long enough to be relatively homogeneously mixed in the troposphere. The radiative forcing of the well-mixed greenhouse gases can be calculated using the simplified empirical formula listed in Table 4.3.4. These expressions (adopted from the IPCC, 2001) are derived from radiative transfer models and generally have an uncertainty of about 10% Butler (2011). It is worth to mention that the contributions from the aerosol and tropospheric ozone are not included in the calculation of radiative forcing of the well-mixed long-lived greenhouse gases. In order to understand the radiative forcing of the trace gases in more simplistic way, the annual green house gas index (AGGI) is defined as the combined radiative effects of well-mixed greenhouse gases produced by both anthropogenic as well as natural sources. An anthropogenic and natural emission can affect several forcing agents.
Table 4.3.4: Expressions for Calculating Radiative Forcing for different well-mixed greenhouse gases.

<table>
<thead>
<tr>
<th>Trace Gas</th>
<th>Radiative Forcing, ΔF (Wm^{-2})</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>ΔF = αln(C/C_o)</td>
<td>α = 5.35</td>
</tr>
<tr>
<td>CH₄</td>
<td>ΔF = β(M^{1/2} - M_o^{1/2}) - [f(M,N_o) - f(M_o,N_o)]</td>
<td>β = 0.036</td>
</tr>
<tr>
<td>N₂O</td>
<td>ΔF = ε(N^{1/2} - N_o^{1/2}) - [f(M_o,N) - f(M,N_o)]</td>
<td>ε = 0.12</td>
</tr>
<tr>
<td>CFC-11</td>
<td>ΔF = λ(X - X_o)</td>
<td>λ = 0.25</td>
</tr>
<tr>
<td>CFC-12</td>
<td>ΔF = ω(X - X_o)</td>
<td>ω = 0.32</td>
</tr>
</tbody>
</table>

(Source: IPCC (2001))

Where the subscript o denotes the unperturbed (1750) abundance i.e. pre industrial era of the gases.

\[
f(M,N) = 0.47\ln[1 + 2.01\times10^{-5} (MN)^{0.75} + 5.31\times10^{-15}M(MN)^{1.52}]\]

C is CO₂ in ppm, M is CH₄ in ppb
N is N₂O in ppb, X is CFC in ppb
C_o = 278 ppm, M_o = 700 ppb, N_o = 270 ppb, X_o = 0

4.5 Summary

The measurements of surface black carbon mass concentrations, particulate matter and trace gases along with meteorological parameters at a tropical urban site Hyderabad show a well defined diurnal variation, is observed at Hyderabad. The diurnal variation of BC has shown a strong association with the local boundary layer dynamics as well as local anthropogenic activities. Several distinct advection pathways were identified on the basis of trajectory clustering. The most important potential sources are found to be the central India and IGP and some hot spots in Pakistan. The Ångström exponent (\(\alpha_{abs}\)) estimated from the spectral values of absorption coefficients (\(\sigma_{abs}\)) are found to vary from 0.92-1.1 indicating high BC/OC ratio is typically of fossil fuel origin over Hyderabad. The annual average BC mass fraction was found to be 10±3 % and contributing to the atmospheric forcing by 55 ± 10 % . The BC ARF at TOA is positive for all month, thus suggesting an overall heating of the regional climate.

The MTS-AOD₅₅₀ and PM₂ showed the similar seasonal-diurnal variation trend except for pre-monsoon season mainly attributed to presence of elevated aerosol layers associated with long-
range transport. Since the PM$_2$ represents the mass concentration of fine-mode particles while AOD represents the columnar aerosol loading contributed from both fine and coarse-mode particles, during pre-monsoon season when the coarse-mode particles (dust, sea-salt) are dominated the correlation coefficient between PM$_2$ and AOD may be reduced on specific cases. The correlation between surface PM$_2$ and columnar AOD is strongly dependent on the variations in the source regions and transportation of aerosol at different altitudes and the presence of multiple structured layers of aerosol at various altitudes having different chemical and physical characteristics. The satellite derived PM$_2$ was found to be well within the uncertainty of measurements.