

# Chapter 1

## Introduction

Atmospheric aerosols affect the global climatic system in many ways e.g. by attenuating the solar radiation reaching the ground, modifying the wavelength dependence of solar radiation within the atmosphere and at the ground, re-distributing the earth-atmosphere energy budget and influencing cloud microphysics and hydrological cycle (IPCC, 2007). Although the aerosol optical properties have been now well known, large uncertainties are still associated with the aerosol-climate coupling due to the variety of the aerosol types, the changing optical and physico-chemical properties, the influence of dynamic and synoptic meteorology and the mixing processes (internal and external) in the atmosphere. The IPCC (2007) report summary indicated large uncertainties in knowledge of aerosol optical and physico-chemical properties particularly over Indian sub-continent and adjoining oceanic regions. Also, the change in the Earth's radiation and energy balance due to aerosols is much more uncertain (and opposite in sign) compared to the greenhouse gases (e.g. Haywood and Boucher, 2000). As a result, considerable scientific effort has been made in the last decade to investigate atmospheric aerosols concerns mainly their effect on global climate. The estimated radiative forcing of the anthropogenic aerosols on a global scale is determined to be  $-0.5 \pm 0.4 \text{ Wm}^{-2}$  (IPCC, 2007). However, this value varies significantly on regional scale due to large spatio-temporal heterogeneities in aerosol characteristics (Kim and Ramanathan, 2008). This in turn has resulted in serious climatic implications such as global dimming, an increase in atmospheric stability, changes in hydrological cycle and rainfall distribution (Lau et al., 2006).

Atmospheric aerosols over Indian sub-continent are a mix of the various types i.e. anthropogenic aerosols from the urban centers, biomass burning from seasonal forest fires and crop residue burning, desert dust produced in Thar desert as well as transported from Arabia and Middle East and the marine aerosols from the adjoining oceans during the southwest monsoon. Due to large diversity in population density, regional emissions, land use and seasonally changing air masses, the aerosol load its optical properties and their climate impact show large variations over India both spatially and temporally (Lawrence and Lelieveld, 2010). Several campaigns e.g. INDOEX, ARMEX, LC-I, LC-II, ICARB, W-ICARB, ARFI, ARFI-RAWEX, CAIPEEX have been carried

out to characterize the continental and oceanic aerosols in the Indo-Gangetic plains, AS and BoB (Ramanathan et al., 2001b; Moorthy et al., 2005, 2009; Jayaraman et al., 2006). However, the periodic campaigns covering the entire Indian sub-continent are essential to study the small scale features, temporal variations, seasonal effects and spatial gradients for the estimation of the climatic impact in terms of changes in radiative forcing, local and regional meteorology and the air-mass origin.

The rapid industrialization in Hyderabad and its growth as a mega city have lead to exponential increase in industrial activity and the general economic prosperity. The emission of black carbon, trace gases and various precursor gases which are emitted from vehicular and industrial emissions have shown large increase in this region. The unique geographical location of Hyderabad (17.47<sup>o</sup> N, 78.58<sup>o</sup> E) in south India, makes it an ideal site for detailed studies of the rich mixtures of aerosol transported from deserts, IGP and the surrounding oceanic regions in addition to the local emissions. The aerosols over Hyderabad are a mix of marine particles, mineral or desert dust (natural), industrial emissions, fossil fuel combustion and automobile exhausts etc.

## **1.1 Atmospheric Aerosols**

Atmospheric aerosols are tiny solid or liquid particulates consist of a wide range of types having different composition, shapes, sizes and optical properties which affect the earth energy budget by scattering and absorbing the solar radiation reaching the ground. Atmospheric aerosols are considered as the most variable atmospheric constituents and the large variability is due to the short residence time (~ 5-7 days), variety of their sources and types, emission rates, mixing processes, transport and deposition mechanisms which result in their spatial and temporal inhomogeneity. The lack of exact knowledge of their contribution to the Earth's radiation budget at any given time is responsible for the current uncertainty associated with the global climate system.

The majority of aerosols found within the boundary layer are associated with the local and regional emissions. However, aerosol layers above the boundary layer height (BLH) are mainly associated with long-range transport and may contribute significantly to the columnar AOD variations. The boundary layer dynamics driven by the local meteorology as well as the local aerosol emissions within the urban environment are the main factors that affect vertical distribution

of aerosols. The vertical distribution of aerosols is very critical in understanding their effect on radiative forcing and climate (Meloni et al., 2005; Moorthy et al., 2009; Koch and Del Genio, 2010) and particularly over the Indian sub-continent, due to the variety of sources, the long-range transport and the mixing processes in the atmosphere and it also influences the thermal gradient between land and ocean that controls the monsoon onset and in cloud formation processes (Lau et al., 2006).

## **1.2 Classification of Aerosols and their Distribution**

Apart from the general category in aerosol discrimination i.e. natural and anthropogenic the aerosols can be divided into four main types depending mainly on their source regions (Dubovik et al., 2002). These are biomass burning (forest fires, agriculture burning, wildfires, etc), anthropogenic aerosols (industries, exhausts, fossil fuel and bio-fuel combustions), marine aerosols (sea salt and natural sulphates) and desert or mineral dust (sand soil, etc). Since each of this source type produces a mix of different chemical species, the resultant aerosol show a characteristic physical and optical properties. For example BC (soot) is ubiquitous and the second most important atmospheric variable after CO<sub>2</sub> (Jacobson 2001) which also complement the green house effect by its strong absorption of the visible spectrum of incoming solar radiation despite their low mass concentration in the atmosphere. The absorption by BC varies weakly with the wavelength. In addition the absorption efficiency of BC aerosols is strongly dependent on the temperature. For example, coal combustion at low temperature produces aerosols with strong wavelength dependence in the absorption efficiency.

### ***Biomass burning***

Biomass-burning aerosols (BBA) are mainly produced by burning of vegetation and can be caused from both natural and anthropogenic origin e.g. lightning, burning of forest and agriculture waste. Biomass burning is the major source of atmospheric particles such as black carbon (BC), organic carbon (OC) and gaseous molecules (including CO, CO<sub>2</sub>, CH<sub>4</sub>, VOC, N<sub>2</sub>O) and it is dominant source of tropospheric aerosols over the tropics. Biomass-burning accounts 40% of the global emission of BC aerosols (Bond et al., 2004). BC content of biomass burning particles has large uncertainty as well as the variability compared to the OC aerosols (Reid et al., 2005). The optical and physical properties of smoke particles from biomass burning vary significantly during transportation and modification processes namely aging and also depends on the phase of the fire

i.e. flaming or smoldering (Eck et al., 2003). The favorable modification processes of BBA in the atmosphere are coagulation and aging. In general, the size distribution of BBA is dominated by the fine mode particles, thus causing large attenuation of the solar radiation at shorter wavelengths. In addition to their crucial role in atmospheric chemistry and biogeochemical cycle, the BBA also have the potential to significantly impact the visibility, air quality, human health and climate by attenuating the incoming solar radiation and heating the lower and middle troposphere, since the dominant BC component is the most absorbing aerosol type, based on satellite observations, Chand et al. (2009) have shown that while absorbing aerosols (BBA) above reflecting clouds darken the scene by enhanced absorption, over a dark surface they tend to brighten the scene by increased backscatter.

### ***Anthropogenic aerosols***

Anthropogenic aerosols are emitted from densely populated and industrialized regions over the globe due to anthropogenic activities and have the greatest climate impact. These aerosols are short-lived and mostly fine particles (size  $<1\mu\text{m}$ ). The main chemical components of anthropogenic aerosols are sulfate, nitrate, organic and inorganic carbonaceous compounds produced by several physical and chemical processes such as gas-to-particle conversion, biomass burning and fossil fuel burning. Since the size of the fine-mode particles is of the order of the wavelength in the visible spectrum of solar radiation. The anthropogenic aerosols substantially modify the incoming solar radiation and are expected to have a stronger climatic impact than the coarse-mode particles.

The main aerosol types over urban environment like Hyderabad are carbonaceous aerosols and these aerosols are complex mixture of organic and inorganic compounds. About 38% of carbonaceous aerosols are originated from biomass burning and the rest from fossil fuels (IPCC 2007). The lifetime of carbonaceous aerosols in the atmosphere is generally driven by wet and dry deposition depending on their hydrophobic or hydrophilic nature. The organic aerosols are emitted either as primary aerosol particles or formed as secondary aerosol particles from condensation of organic gases and contribute 20-50% to the total fine aerosol mass at continental mid-latitudes (Putaud et al., 2004) and as high as 90% in the tropical forest areas (Andreae and Crutzen, 2007). A substantial fraction of the organic aerosols is water soluble and constitute the efficient cloud condensation nuclei (CCN) which is the important sink for organic aerosols. The optical

properties of organic aerosols depend on the mixing of organics with other aerosol components and therefore, they are highly variable. Some of the organic aerosols produced from fossil fuels are relatively weakly absorbing but do absorb solar radiation at some ultra violet and visible wavelengths (Bond et al., 2001). However, organic aerosol from high-temperature combustion such as fossil fuel burning appears less absorbing than those arising from low-temperature combustion such as open biomass burning (Kirchstetter et al., 2004). In general, the anthropogenic aerosols can be highly absorbing or scattering depending on their composition. Absorbing aerosols produced by different sources i.e. biomass burning or urban emissions can be further distinguished by different wavelength dependence in light absorption with the former having much stronger wavelength dependence (Kirchstetter et al., 2004).

The sulfate particles are mainly produced by the aqueous phase reaction within cloud droplets by oxidation of  $\text{SO}_2$  via gaseous phase reaction with OH and by condensational growth onto pre-existing particles (Penner et al., 2001). The dominant source of sulfate particles is the fossil fuel burning with some small contribution from biomass burning. However, sulfate aerosols are also produced by natural sources, such as dimethyl sulphide (DMS), marine phytoplankton and volcanoes. The estimated residence time of  $\text{SO}_2$  defined as the ratio of the global burden to its global emission flux, ranges from 0.6 day to 2.6 days as a result of different deposition parameterizations; the global turnover time of sulfate is 4 to 7 days (IPCC 2001). The size distribution of sulfate aerosols is strongly depended on the nucleation, condensation and coagulation processes in the atmosphere. Sulfate is a scattering type particle in contrast to BC and a key climate variable. The model estimated global annual mean radiative forcing of sulphate aerosols, biomass burning aerosols, fossil fuel organic carbon and black carbon aerosols are  $-0.4 \text{ Wm}^{-2}$  ( $-0.2$  to  $-0.8 \text{ Wm}^{-2}$ ),  $-0.2 \text{ Wm}^{-2}$  ( $-0.07$  to  $-0.6 \text{ Wm}^{-2}$ ),  $-0.10 \text{ Wm}^{-2}$  ( $-0.03$  to  $-0.30 \text{ Wm}^{-2}$ ) and  $+0.2 \text{ Wm}^{-2}$  ( $+0.1$  to  $+0.4 \text{ Wm}^{-2}$ ) respectively (IPCC 2007).

### ***Marine aerosols***

The marine aerosols are composed of both natural and anthropogenic constituents such as liquid sea water drops, dry sea-salt particles, dust and minerals transported from the continental origin and from volcanoes, biological particles (bacteria, viruses), sulfate, nitrates, ship exhaust emissions and soot. The marine aerosols are generated by several processes such as gas-to-particle conversion, nucleation, condensation and their size ranges from nanometers to millimeter.

However, the interaction of sea-salt with gaseous molecules acts as a sink, suppresses the formation of new particles and modify their size distribution. Sea-salt is the primary marine aerosol formed by the bursting of air bubbles through the wind wave interaction in the atmospheric boundary layer over the ocean. After emission in the atmosphere sea-salt particles can be internally and externally mixed with other particles and their size ranges from less than  $0.1\mu\text{m}$  to greater than  $10^3\mu\text{m}$ . The physical and optical properties of sea-salt aerosols show wide variations and these strongly depended on the meteorological conditions particularly the wind speed and relative humidity. Since the  $2/3$  of the Earth's surface is surrounded by the ocean, sea-salt particles significantly contribute to the total amount of the tropospheric aerosols. The estimated particulate mass varies from  $0.3 \times 10^{12}\text{kg}$  to  $30 \times 10^{12}\text{kg}$  corresponding to sea-salt mass flux of  $0.03 \times 10^{-6}$  to  $3 \times 10^{-6} \text{ g m}^{-2}\text{s}^{-1}$ . Sea salt aerosol particles have varied climate impact and these act as CCN, modify the cloud microphysics and play an imperative role in cloud development over the ocean. The large concentration of these particles also scatter the incoming solar radiation and substantially affect the marine chemistry, geochemistry, biochemistry, visibility and satellite remote sensing. However, the quantitative impact of sea salt particles on atmospheric processes depend on several factors such as their chemical composition, size, concentration, mean residence time, vertical distribution, optical properties and underlying meteorological conditions. The model estimated global annual mean of sea salt's short wave indirect effect (annual mean  $-0.38 \text{ W m}^{-2}$ ) was found to be less than its direct effect (annual mean  $-0.65 \text{ W m}^{-2}$ ). However, sea salt's indirect effect was found to be far stronger over the Southern Hemisphere than over the Northern Hemisphere (Ayash et al., 2008).

### ***Dust aerosols***

Mineral dust is a mixture of carbonates, sulfates, organic material and soot particles constituting one of the largest sources of tropospheric aerosols with global load of  $2150 \text{ Tg/yr}$ , about 37% of the total production of atmospheric primary aerosols by both natural and anthropogenic sources (Penner et al., 2001). Mineral-dust aerosols are produced mainly by wind erosion of desert soils, lifted to high altitudes by convection and which can be transported over long distances from their source regions and mixed with continental aerosols such as sulfate, nitrate and soot etc. thus playing an important role in the heterogeneous chemical reactions (Ginoux et al., 2001). The global average age of dust at deposition agrees with residence time of  $\sim 2.7$  days, while dust in the atmosphere is on average twice as old (Han and Zender, 2009). Similar to the sea-salt, mineral dust

aerosols consist of both soluble and insoluble components and exhibit a wide range of physical and optical properties. However, these are coarse-mode particles and show a weak spectral dependency. The atmospheric residence time of a dust particle (having radii between 0.1 and 1.0 $\mu\text{m}$ ) is strongly dependent upon its size and shape. Dust particles are removed from the atmosphere by gravitational settling, dry deposition, wet deposition and rain washout and most dust particle falls into the oceans where it becomes a nutrient source. The mineral aerosols play a crucial role in the atmospheric phenomena by acting as CCN, influencing the local and global atmospheric dynamics and photochemical processes, suppressing the precipitation, modifying the Earth's radiation budget, attenuating the visibility and harming the human health (Rosenfeld et al., 2008). The model estimated global annual mean radiative forcing of mineral dust aerosols was found to be 0.6 to +0.4  $\text{Wm}^{-2}$  (IPCC 2001).

### ***Distribution of Aerosols***

The major sources for anthropogenic sulfate, organic and BC aerosols are the densely populated and industrialized regions of northern latitudes such as eastern US, Europe, south and east Asia. The major source regions for natural sulfate and sea salt aerosols are the global oceans, while the dust is mainly defined over the desert areas over the globe. The total optical depth observed to be larger over East Asia due to the combined effects of both natural (dust) and anthropogenic emissions and over South Asia and Sahara due to dust aerosols. Table 1.1.1 summarizes the production mechanisms in different sources and their relative strengths of the natural and anthropogenic component of aerosol.

Table 1.1.1: *Sources, source strength, production mechanism and particles components of the natural and anthropogenic aerosols [Source: d’Almeida et al. (1991) and Hobbs (1993)].*

| <b>Source</b>                 | <b>Production Mechanism</b> | <b>Aerosol Component</b> | <b>Source Strength<br/>(10<sup>12</sup>g/yr)</b> |
|-------------------------------|-----------------------------|--------------------------|--|
| <b>Anthropogenic</b>          |                             |                          |  |
| Direct-emission               | Direct-injection            | Dust/Soot/Water-soluble  | 10-90  |
| Biomass Burning               | Combustion                  | Soot                     | 3-150  |
| Gas-to-particle<br>conversion | Nucleation                  | Sulfate/Nitrate/Organics | 175-325  |
| <b>Natural</b>                |                             |                          |  |
| Extraterrestrial              | Cosmic dust                 | Meteoric dust            | 10   |
| Biosphere                     | Direct-injection            | Pollen/Spores            | 80   |
| Volcanoes                     | Direct-injection            | Water-soluble            | 15-90  |
| Biomass Burning               | Combustion                  | Soot                     | 200-450  |
| Gas-to-particle<br>conversion | Nucleation                  | Sulfate/Nitrate/Organics | 345-1100   |
| Ocean/Fresh water             | Bubble bursting             | Sea-salt                 | 1000-2000  |
| Crust/Cryosphere              | Weathering                  | Soil dust                | 2000   |
| Cloud processing              | Clouds evaporation          | Water-soluble            | 3000   |

### 1.3 Properties of Atmospheric Aerosols

#### 1.3.1 Physical Properties of Atmospheric Aerosols

##### *Size Distribution*

The size distribution of aerosols is a key parameter which characterizes the aerosol physical and optical properties at any place. These distributions are shaped by several dynamical processes namely advection, convection, turbulent mixing, humidification, nucleation, condensation, coagulation, cloud contamination, scavenging by precipitation, long-range transport and the photochemical production of secondary aerosol particles. The distribution analysis can be applied to their number or volume and is best fitted either by power-law, lognormal or composite functions (*equations 3.1.1 and 3.1.2*). The power law distribution is valid for monodisperse aerosol system i.e. the number concentrations of aerosols decrease drastically with radius and shows a narrow size distributions and lower geometric standard deviation values. However, nature does not support the

monodisperse distribution and therefore, the aerosols in the atmosphere are polydisperse, which result in wider size distributions with higher standard deviation values due to wide variety of sources and generally follow the lognormal distribution. The lower and upper size limits of aerosols are from few nanometers to  $\sim 100\mu\text{m}$  and their properties change substantially over this size range. Depending on the size, aerosols are classified into three categories i) Aitken nuclei mode ( $\sim 0.001$  to  $0.1\ \mu\text{m}$ ), ii) accumulation mode ( $\sim 0.1$ – $1.0\ \mu\text{m}$ ) and iii) large mode/giant particle  $> 1.0\ \mu\text{m}$ . Alternately, these are also labeled as fine/sub-micron aerosols (size  $< 1\ \mu\text{m}$ ) and coarse-mode aerosols (size  $> 1\ \mu\text{m}$ ). The aerosol size distribution can be used as proxy to infer the relative contribution of aerosols from different sources.

### ***Morphology of Atmospheric Aerosols and their Size***

Morphology of aerosol particles determines their chemical (i.e. reactivity), physical (e.g. aging, size, sphericity) and optical properties (e.g. scattering and absorption efficiency of light). Fu et al., (2012) suggested that soot particles showed a modified morphology and attributed to atmospheric aging. The irregular geometry and complex microstructure of soot aggregates may provide active sites for deposition of common atmospheric gases such as  $\text{O}_3$ ,  $\text{NO}_2$  and  $\text{SO}_2$ , which could readily oxidize soot surfaces (Decesari et al., 2002). The reaction rates of aerosol particles with gas-phase species can vary by several orders of magnitude depending on the morphology of the particle (Garland et al., 2009). Morphology of aerosol plays an important role for the determination of their sources, transport, deposition, optical and physical properties. It can be used as a surrogate for the source apportionment of aerosol. For example, soot and sulfuric acid aerosols are in the Aitken mode, while biomass burning and anthropogenic aerosols (ammonium, sulfate) in the accumulation mode. Larger aerosols are the naturally-produced particles i.e. dust and sea salt which are in general non-spherical particles. Since the drag force and thereby the transport rates of aerosol particles are affected by their morphology, these transport rates determine their atmospheric residence time and pattern of deposition in the lung where the aerosols deposit, therefore, it is also useful for epidemiological and air quality studies.

### ***Refractive Index***

Refractive index is a key parameter which determines the scattering, absorption and also the size distribution of aerosols. It depends on the humidity, types of aerosol originated from different sources and their modification processes. The most hygroscopic aerosol species are ammonium sulfate, sea salt and ammonium nitrate. The refractive index of hygroscopic aerosols changes with

the additional amount of water absorb from the ambient in response to changing relative humidity. The changes in refractive index are associated with the change in specific density, size and mass fraction. The small changes in the refractive index of aerosol particles can change/or flip the sign of its radiative impact. For example, changes in refractive index values from  $n=1.75+0.44i$  to the medium values of  $n=1.85-0.71i$  alters the annual-mean short-wave anthropogenic aerosol forcing clear-sky from  $-0.65\text{Wm}^{-2}$  to  $-0.53\text{Wm}^{-2}$  and all sky from  $-0.27$  to  $-0.13\text{Wm}^{-2}$  (Stier et al., 2007). The typical refractive index of aerosol in different atmospheres (urban, rural and ocean) is summarized in Table 1.2.1. The large value of the real part in the refractive index of polluted air masses (i.e. urban aerosol) are predominantly caused by the high abundance of metal oxide/hydroxide particles, the high imaginary parts by high abundances of soot (Ebert et al. 2004).

**Table 1.2.1:** Summary of refractive index of aerosol for different atmospheres.

| Studies   | Refractive Index                            | References               |
|---|---|--------------------------|
| Small urban aerosols at RH close to 50%   | 1.56–0.08i                                  | Shettle and Fenn (1979)  |
| Urban aerosols (Pune, India)  | 1.55-1.60                                   | Pandithurai et al., 1996 |
| Urban aerosols (Germany)  | 1.6 -1.73–(0.034–0.086)i                    | Ebert (2004)             |
| Mean value over 19, 20 and 31 July 2000 in Paris area                             | 1.51(±0.02)–<br>0.017(±0.003)i              | Raut and Chazette (2008) |
| Rural aerosol (Kleiner Feldberg, Germany)   | 1.54–1.61-(0.001–0.021)i                    | Ebert (2004)             |
| Amazonian Tropical Rainforest site (Biomass burning aerosol)                      | 1.41-0.013i                                 | Guyon et al., 2003       |
| Tropospheric aerosols in Oklahoma: Dry aerosols                                   | 1.4–1.5(±0.05)                              | Ferrare et al. (1998)    |
| Tropospheric aerosols in Oklahoma: Wet aerosols                                   | 1.37–1.4                                    | Ferrare et al. (1998)    |
| Pollution plumes advected from the European continent out over the Atlantic Ocean | 1.56(±0.1)–i0.009 (±one order of magnitude) | Muller t al. (2002)      |
| Over Atlantic Ocean   | 1.33–1.45–i0.001–0.008                      | Redemann (2002)          |

### 1.3.2 Chemical Characteristics of Atmospheric Aerosols

Aerosols are composed or mixed of wide variety of chemical compositions such as inorganic ( $\text{Al}^{+3}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{+2}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ ), elemental carbon (soot) and organic carbon. The organic aerosols are mostly non hygroscopic (non soluble), while the inorganic aerosols are hygroscopic (i.e. soluble in water) in nature which determine their ability to act as a cloud condensation nuclei. The hygroscopicity of aerosols can modify their properties and radiative impact. It can also lead to large uncertainties in satellite retrieved aerosol properties. Kaufman et al., [2005] estimated an uncertainty upto 0.02 in monthly averaged AOD retrieved from MODIS over Ocean and attributed to the hygroscopic growth of sea-salt particles. Similarly, an uncertainty was found up to 20-40% due to hygroscopic growth of smoke particles over Boreal land (Wong and Li, 2002). The current existing models use fixed time scale of 1-2 days to convert hydrophobic aerosols into hygroscopic aerosols. However, the mixing of BC and organic aerosols with hygroscopic aerosols take place in a few hours depending on location, season and photochemical reaction (Ervens et al. (2010); Wang et al., (2010)). Particle growth due to its hygroscopic nature and thereby gravitational settling rates are enhanced by the solubility (Zhang et al., 2005). Hsu et al., (2005) reported the solubility of seawater mineral aerosol components in the order  $\text{Al}$  (1.3%) =  $\text{Fe}$  (1.1%)  $\leq$   $\text{Pb}$  (20%)  $\leq$   $\text{Cu}$  (27%)  $\leq$   $\text{Mn}$  (43%)  $\leq$   $\text{Zn}$  (45%)  $\leq$   $\text{Ni}$  (50%)  $\leq$   $\text{Cd}$  (69%) and attributed to different degrees of contribution of anthropogenic aerosols. The solubility is further correlated with particle size, for example, higher solubility of Fe in fine mode than in coarse mode (Baker and Jickells, 2006). The inorganic aerosols such as  $\text{NH}_4^+$ ,  $\text{SO}_4^-$ , elemental carbon and transition metals mostly constitute the fine mode particles whereas the coarse mode particles are dominated by  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$  etc. However, aerosol such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are ubiquitous in the urban environment and are found both in fine and coarse particle modes, with two prominent peaks in fine mode size range (0.1-1 $\mu\text{m}$ ) [Seinfeld and Pandis; 1998].

Apart from the individual characteristics of each aerosol, their mixing of several species further complicates its radiative impact. For example, BC can absorb the light two times larger when it is mixed with scattering particles such as  $\text{SO}_4^-$  and  $\text{NO}_3^-$  as compared with their individual (IPCC III; 2001). The uncertainty in transition from external to internal mixing of absorbing forest fire and non-absorbing background particles introduce an uncertainty in the plume's radiative forcing

by a factor of 5-6 (Fiebig et al., 2003). The mixing state of aerosol controls the influence of other aerosol parameters on activation of cloud condensation nuclei (CCN), for example, Dusek et al., (2006) reported that CCN strongly depends on particle size distribution. Ervens et al., (2010) reported that the size-resolved chemical composition and mixing state are required for predicting CCN close to pollution sources. However, to what extent mixing state and chemical composition of aerosol can impact the activation of CCN needs to be addressed and included in the global climate model. Medina et al. (2007) reported a 35% over prediction in CCN for semi-urban air masses at New Hampshire even when size-resolved aerosol composition is employed and attribute the over-prediction to the assumption of an internal mixing. Since each source region emits particles with different chemical characteristics and which in turn gives rise to different signature in physical and optical properties of aerosol particles, these can be also used as atmospheric tracer.

### **1.3.3 Dynamical Properties of Atmospheric Aerosols**

The formation and evolution of atmospheric aerosols are key processes describing and determining their dynamics (Kulmala et al., 2000). Once the aerosol particles are formed, they undergo various physical and chemical processes namely nucleation, condensation, coagulation, gas-to-particle conversion, transportation and scavenging leading to changes in physical and optical properties of aerosol, which are important variables and need to be considered in the climate models. These processes also lead to the well mixing (internal and external) of the aerosols in the atmosphere and therefore, a single aerosol type does rarely exist at any site in the globe.

#### ***Nucleation***

Nucleation is the ubiquitous process in the atmosphere that leads to the formation of freshly nanometer-size particles and subsequent growth to larger size ranges and it is affected by magnitude of solar radiation (Kulmala 2003). It plays an important role in several processes, such as cloud radiative properties, cloud lifetimes, precipitation rates and consequently rain formation and freezing. The transition from one phase to another during nucleation processes does not occur instantly due to the enthalpy difference between these two phases (Schneider and Voigt 2010). However, as the enthalpy barrier is crossed, the nucleation cluster is formed and it grows very rapidly. The nucleation can be both homogeneous and heterogeneous. The homogeneous nucleation takes place by the condensation of precursor gases at super-saturation levels and creates new particles in the air with low initial aerosol concentration. The heterogeneous nucleation takes

place when gaseous molecules condense onto pre-existing solid or liquid particles at significantly lower effective super-saturation.

### ***Coagulation***

The growth mechanism of aerosol particles by aggregation, results from the differences in the speed and direction of moments of the aerosol in the atmosphere. The coagulation of aerosol particles significantly modifies their shape and size distribution in the atmosphere and reduces the number concentrations while the total mass of particles is conserved without changing the chemical compositions. Another important characteristic of coagulation processes is the change in the mixing state of particles. Since the aerosol particles originate from different sources they have different size and chemical compositions as well as optical properties. Therefore, coagulation between unequal-sized particles will convert to internally mixed aerosols and consequently changes the optical properties and hygroscopic growth characteristics of the particles (Levin and Cotton, 2009). The coagulation is the efficient mechanism for the formation of fine and accumulation-mode aerosols in the atmosphere. If the initial distribution of particles is known, the coagulation rate is a function of the mechanism bringing the particles together. There are several coagulation mechanisms that affect the coagulation rate namely Brownian, gravitational, convective Brownian diffusion enhancement, turbulent inertia and turbulent shear coagulation. Coagulation with larger particles serves as a significant sink for newly formed nuclei mode particles.

### ***Condensation***

Condensation is an efficient growth mechanism in which aerosol particle grows by taking up vapors from the gas phase. It is the first-order transition of physical state of matter from the gaseous to liquid or solid phase. The condensational growth rate of a single particle is proportional to particle surface area or to the particle diameter and it is more effective in the size range of  $< 0.1 \mu\text{m}$ . As a result the particle size distribution becomes narrower (Levin and Cotton, 2009). The most condensable gases are sulphuric and nitric acid, ammonia, water and various organic compounds. The atmospheric residence time of ultra fine particles are determined by their condensation properties.

### ***Gas-to-Particle conversion***

This mechanism is an important process for the formation of fine particles by converting volatile gases into the condensable species. There are numerous mechanisms for the formation of aerosol

particles through gas-to-particle conversion such as: (i) reaction of gases to form low vapor pressure products e.g. the oxidation of sulfur dioxide to sulfuric acid, (ii) single or multi-component nucleation of low pressure vapors, (iii) vapor condensation onto surfaces of pre-existing particles, (iv) reaction of gases at the surface of existing particles, (v) chemical reaction within the particles. Among these mechanisms, the (i), (iv) and (v) affect the composition of both vapor and liquid phases, while (ii) initiates the actual phase transition and increases the aerosol particle number concentration and (iii) increases the aerosol mass (Spurny et al., 2000). The efficiency of gas-to-particle conversion process is strongly dependent on the concentration of the species, their thermodynamic and nucleation properties.

The formation and growth of atmospheric aerosol particles strongly depend on the geographical location and meteorological conditions as well as the different altitude layers in the atmosphere (boundary layer, troposphere and stratosphere). The formation rate of fine mode particles of size 3nm ranges from  $0.01-10\text{cm}^{-3}\text{s}^{-1}$  in the boundary layer,  $10^2\text{cm}^{-3}\text{s}^{-1}$  in the urban regions and  $10^4-10^5\text{cm}^{-3}\text{s}^{-1}$  in coastal and industrial plumes. However, the typical growth rates in the in the mid-latitudes and polar regions are  $1-20\text{nm s}^{-1}$  and  $0.1\text{nm h}^{-1}$  respectively (Kulmala et al., 2004).

### ***Deposition***

Aerosol particles produced by several physical and chemical transformations such as nucleation, condensation, coagulation and gas-to-particle conversion are eventually scavenged from the atmosphere by dry and wet deposition. The dry deposition is the most efficient removal pathway for coarse mode ( $2.5\mu\text{m}<dp<10\mu\text{m}$ ) and ultrafine mode ( $dp<0.1\mu\text{m}$ ) particles. In wet deposition mechanism the particles are removed from the atmosphere by rain or fog and it is the most efficient removal pathway for fine particles, particularly particles in the size range  $0.1-1\mu\text{m}$ . The wet deposition is caused by the absorption of aerosol particles by a condensed phase such as a water cloud droplet or rain drop. The two major wet deposition mechanisms are nucleation scavenging i.e. cloud condensation nuclei (CCN) and occult i.e. deposition by the fog and cloud droplets. The removal rate of the wet deposition is strongly dependent on the fall velocity, size distribution of the droplets and collision efficiency between droplets and aerosol particles.

### ***Gravitational Settling***

It is an efficient removal mechanism in which the coarse aerosol particles are scavenged by the gravity. The settling velocity is proportional to size and mass of particle. The effect of Brownian

motion on coarse mode particles such as sea-salt and dust is weak as compared to gravitational settling and these particles fall out rapidly from the atmosphere. However, the effect of Brownian motion is of the order of magnitude as the gravitational settling for fine mode particles such as sulfate, black carbon etc. and these particles can not be easily removed from the atmosphere and sustained there for longer time. The gravitational settling can lead to dry deposition of the particles.

### ***Long Range Transport***

Since the time span for air parcels to circle the Earth by the prevailing winds in the troposphere is of the order of magnitude of the residence time of the atmospheric aerosols i.e. about a week and therefore, each region over the globe is influenced by the transportation of aerosols from non-local sources. Long-range transport contributes to the mixing state of aerosols over a specific location and it also causes the large heterogeneity in the vertical structure of the atmospheric aerosols and can enhance the new particle formation (Nilsson et al., 2001). The observation of the significant continental aerosol presence over the downwind oceanic regions is mainly due to long range transport. The local and synoptic meteorology and the wind patterns are the major factors that control the long-range aerosol transport. It is an important atmospheric process which substantially modifies the physical, chemical and optical properties of aerosols and their distribution and consequently the Earth's radiation budget.

### **1.3.4 Optical Properties of Atmospheric Aerosols**

The interaction of aerosols particles with radiation determines its impact on the Earth's climate and atmospheric visibility. These effects are controlled by the optical properties of aerosols such as scattering and absorption, aerosol optical depth (AOD), single scattering albedo (SSA), phase function and asymmetry parameter. The effect of particle size on scattering is inferred by a physical term called size parameter (i.e. no of wavelengths that is allowed to fit into a circle of given radius) defined as  $x=2\pi r/\lambda$ , where  $r$  is the particle radius. The criteria for molecular (Rayleigh) and aerosol (Mie) scattering are  $x < 1$  and  $x \sim 1$  respectively. The scattering coefficient of aerosol particles depends on its size distribution and refractive index. Depending upon the chemical composition of aerosols, these can also absorb the radiation and convert into another form of energy and consequently heat the atmosphere. The strong increase in atmospheric

absorption of solar radiation could be due to presence of large concentrations of absorbing mineral dust or soot (black carbon aerosols). In general, the absorption efficiency increases with the refractive index and size of the particles and is a strong function of the chemical composition of aerosols. Using GEOS-CHEM model, Martin et al., (2003) demonstrated the net effects of aerosols on photolysis [ $O_3 \rightarrow O(^1D)$ ] on global scale and found that the scattering and absorption of radiation by aerosol particles decrease the photolysis rates by 5% over dust dominated region in the Northern hemisphere whereas in the biomass burning regions the photolysis frequency decreases by a factor of 2, attributed mostly to BC.

The extinction coefficient ( $\beta$ ) is defined as the fraction of energy removed, per unit path length from an incident wave by a collection of particles. Therefore, the spectral extinction contains information about the particle number concentrations and their size distribution. The aerosol optical depth, which is the integrated extinction coefficient over a vertical column of unit cross section, is a strong function of the abundance, size distribution and complex refractive index of the aerosols present in the vertical column of the atmosphere. The spectral dependency of AOD contains information about the relative dominance of fine and/or coarse mode particles, the aerosol source regions and is an important parameter for the study and modeling of aerosol radiative effects and air quality by monitoring of the particulate matter. The global mean AOD value at 550nm measured over Land and Ocean by Advanced Along Tracking Scanning Radiometer are 0.195 and 0.137 respectively (Bevan et al. 2011). The aerosol optical depth at any height can be computed as:

$$\tau(\lambda, h) = \int_h^{\infty} \beta_{ext}(\lambda, h) dh \quad (1.2.1)$$

Single Scattering Albedo (SSA) is refers to the relative contribution of scattering over absorbing type aerosols particles. It is the ratio of scattering to the total extinction and it infers the efficiency of scattering nature of aerosol particles. SSA is wavelength dependent and contains the information about the chemical composition of aerosols in the atmosphere. The value of SSA varies from ~0.2 for absorbing type aerosols, such as soot to ~1 for scattering type aerosols such as sea salt and sulfate. An increase in SSA value with wavelength can be associated with the dominance of coarse-mode desert dust particles in the aerosol size distribution, while decrease of SSA with wavelength is characteristic for biomass burning and anthropogenic aerosols. Duboik et al., (2001) reported the spectral variation of SSA at different wavelength 0.44, 0.670, 0.87 and 1.2

$\mu\text{m}$  for three different aerosols types including urban-industrial mixed, biomass burning and desert dust and the marine aerosols to be  $(0.98,0.97,0.96,0.95)\pm 0.02$ ,  $(0.94,0.93, 0.91,0.90) \pm 0.02$  and  $(0.92,0.95,0.96,0.97) \pm 0.03$  respectively.

The phase function determines the angular distribution of the scattered energy and it is expressed as:

$$P(\theta) = \frac{\beta(\theta)}{\beta_{sc} / 4\pi} \quad (1.2.2)$$

Where  $\beta(\theta)$  and  $\beta_{sc}$  are the angular and total scattering cross sections of aerosol particles respectively. The diverse sources and strengths of atmospheric aerosols lead to variety of size modes (nucleation, fine and coarse), complex refractive index and the phase functions. The phase functions are quite different for the different kind and size of aerosol particles. The phase function is higher for larger size particles at smaller scattering angles. The large differences in phase function at higher scattering angles arise due to the contribution from the fine mode particles. The phase function of the atmospheric aerosol at scattering angles greater than  $90^\circ$  is important for the several applications such as satellite remote sensing, atmospheric corrections and climate forcing (Kokhanovsky, 1997). The asymmetry factor ( $g$ ) in the scattering processes measures the difference in amount of radiation between forward and backward scattering along the direction of incident beam and is defined as:

$$g = \frac{\int_{-1}^1 P(\lambda, \theta) \cos \theta d(\cos \theta)}{\int_{-1}^1 P(\lambda, \theta) d(\cos \theta)} \quad (1.2.3)$$

The value of  $g$  can vary in the range of  $-1$  to  $+1$  for complete backscatter and forward scattering respectively, while it is zero for isotropic or symmetric scattering.

## 1.4 Impact of Atmospheric Aerosols

Atmospheric aerosols complement the greenhouse warming by absorption of radiation and also offset it by scattering of incoming solar radiation, have strong impact on both the life and climatic condition on our planet. The intense global investigations on aerosol monitoring and modeling have been taking place during the last few decades in order to understand the complex and

heterogeneous characteristics of atmospheric aerosols and to address their considerable influence on several topics.

### ***Health and Environmental Effects***

The urban aerosols, mainly the fine-mode particles containing a complex mixture of sulfate, soot and smoke (organic and inorganic substances) with aerodynamic diameter less than 2.5  $\mu\text{m}$  have adverse impact on human health and the visibility. Epidemiological and toxicological studies have indicated various deleterious health effects such as respiratory, allergic diseases, childhood asthma etc. due to degradation of air quality by atmospheric aerosols particularly fine and ultrafine particles in major polluted megacities (Pope et al., 2002; Nastos et al., 2010).

### ***Climatic Effects of Aerosols***

Aerosols have large impact on several atmospheric variables and processes, such as significant attenuation of UV radiation, significant contribution in atmospheric heterogeneous chemical reactions, influence in the vertical temperature profile and atmospheric stability, scattering and absorption of solar radiation, modification of the Earth-atmosphere energy budget, acting as CCN, contribution in changes of the cloud microphysical properties such as albedo, lifetime, optical depth as well the hydrological cycle.

Atmospheric aerosols play a vital role in the radiation budget of the Earth-atmosphere system, both directly and indirectly and their quantitative impact is a function of several parameters such as aerosol properties and types (i.e. chemical composition, scattering or absorbing), size distribution and dynamical processes, reflecting properties of the surface, altitude distribution of aerosols and their relative position with respect to that of clouds, solar declination and geographical location. Since aerosols scatter and absorb the incoming solar radiation (direct effect), these can cool the Earth's surface. However, the absorption of light due to aerosols in the lower troposphere heats the air and may cause changes in the vertical temperature profile and the stability of the atmosphere and suppress the convection (semi-direct effect) (Ackermann et al., 2000). Aerosols can also modify the cloud droplet size distribution thereby changing the radiative properties and lifetime of clouds, the so-called first indirect effect (Twomey, 1977). The second aerosol indirect effect is associated with the limitation of collision and coalescence of small droplets inhibiting the growth of cloud drops to rain drops (Rosenfeld, 2000). Both the direct and indirect effects depend on the surface area which is a function of number concentration and size of the particles respectively. A

schematic of the aerosol impact pathways is shown in Fig. 1.3.1. A complete feedback cycle exists in nature in which the changes in the solar radiation caused by the aerosols alter cloud formation, precipitation atmospheric water cycle as well as aerosol chemistry and transport properties.

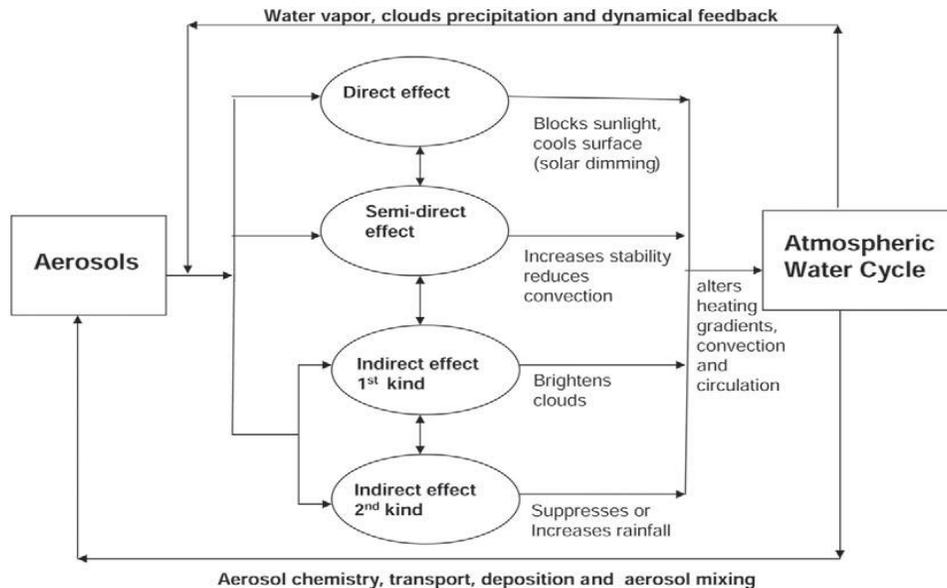


Figure 1.3.1: Schematic of interaction pathways for aerosol local forcing (direct, semidirect and indirect effects) and their response to the Earth atmospheric system (Source: Lau et al., 2008).

### ***Atmospheric corrections for satellite remote sensing***

Satellite remote sensing is an essential technique for global survey, exploration of Earth's atmosphere as well as its resources. The radiation reflected from the Earth's surface undergoes various processes, such as scattering and absorption by aerosols and trace molecules, before it reaches the satellite sensors. Aerosols thus play a major role in determining the response function of the instruments due to their complex nature which becomes more significant when monitoring the properties of land mass through multi-spectral images satellite data. The characterization of spectral dependency of aerosol properties is therefore extremely important for applying the correction to the remotely monitored data.

## **1.5 Importance of Aerosol studies over south Asia and India**

A large fraction of global load of atmospheric aerosols originates in the Southeast Asian region, mainly due to large population density, industrial activity and its tropical location. Large volcanic activity in the region further adds to large scale variability in aerosols fluxes in this region.

Discovery of atmospheric brown clouds during INDOEX campaign further highlights the need of synoptic scale studies to understand and characterize the temporal and optical behavior of the local aerosols. This detailed study over south Asia that examine fluctuations in atmospheric temperature, radiative forcing, snow and ice-cover, precipitation re-distribution, frequency and intensity of tropical cyclones and desertification is the key scientific problem. The long range transport plays a vital role in loading/trend and the optical and physical properties of aerosol of a given place. The climatic effect of aerosols is closely related to their optical properties and the most important among these are the aerosol optical depth and surface albedo. Therefore, the climate response to the different aerosol types varies significantly from negative (cooling) to positive (heating). The multiple platform measurements, such as ground-based networks, ships, aircrafts, balloons and satellites as well as numerical modeling are necessary to reduce these uncertainties.

Even though the natural aerosols play a crucial role in the global climate, the anthropogenic aerosols play a crucial role in regional scales under favorable meteorological conditions different types of aerosols can be advected over a region resulting in some signatures on the columnar AOD and optical properties at any site (Satheesh and Moorthy 2005). The columnar aerosol properties therefore represent the resultant mixture of different aerosol types and show the seasonal changes in their nature associated with the synoptic meteorology consequently impact the radiative forcing (Kim et al., 2010). The mega city of Hyderabad constitutes an excellent atmospheric laboratory for examining the optical and microphysical aerosol characteristics, since it is affected by locally-produced anthropogenic aerosols and naturally-produced particles that transport large distances before reaching the site. In addition, the seasonally changing air masses and the meteorological parameters also strongly affect the aerosol load and properties over the urban site (Kaskoutis et al., 2009).

## **1.6 Objective**

The present study addresses the seasonal and temporal variation of aerosol characteristics as well as their modifications, vertical variations and their radiative impact over the urban area of Hyderabad, India have been studied in detail.

1. Study of seasonal, spatial and temporal variations of aerosol characteristics in view of the air-mass trajectories, meso-scale and synoptic scale atmospheric processes in order to highlight the seasonality in atmospheric composition over Hyderabad from regional and surrounding regions.
2. Despite the fact that the aerosol columnar properties as well as the surface BC concentrations are well examined and continuously monitoring over India, significant gaps in the scientific knowledge about the vertical aerosol profiles still exist which is the key variable for the accurate assessment of aerosol radiative impact. In this regard, lidar observations over Hyderabad are examined on a yearly basis for the investigation of the vertical profiles of aerosols on monthly and seasonal basis.
3. Investigation of natural and anthropogenic sources of aerosols and their distribution, removal, transport mechanisms and dynamics that affect the regional air quality over Hyderabad and over South Asia, also causing considerable atmospheric heating/cooling effects.
4. Emphasis on analysis of BC, the optically absorbing part of soot aerosols which is responsible for large climate implications over south Asia due to the formation of the atmospheric brown clouds.
5. Since the long range transport of aerosol from adjoining ocean and Indian peninsula forms an important component for the observed variability in aerosol characteristics over Hyderabad. The surface, vertical and columnar aerosol properties over Bay of Bengal during winter (2009) as well as the climatology of aerosol over the South Asia region during the last decade (2000-2010) were also examined.

The thesis is organized into seven chapters. Chapter-1 introduces the aerosol physical and optical properties, types as well as their radiative impact. It also includes the current state of the scientific knowledge about atmospheric aerosols over urban Hyderabad and South Asia and highlights the contribution and goals of the present thesis. The site description, measurement techniques and data Analysis are presented in Chapter-2. Chapter-3 addresses the columnar and vertical aerosol properties and their seasonal variability over Hyderabad. The measurements of particulate matter and trace Gases over Hyderabad are presented in Chapter-4. Chapter-5 deals with the study of seasonal aerosol properties over oceanic regions around India which impact the aerosol properties measurements at Hyderabad. The classification of aerosols and their radiative forcing are presented in Chapter-6. Chapter-7 summarizes the accomplishment of the thesis and outlines the future scope.