Chapter 1

Introduction

Earth is surrounded by a thin blanket of life-giving gaseous envelope named atmosphere. The envelope of air that surrounds the Earth is composed of \(~ 78\% \) nitrogen and \(21\%\) oxygen by volume. The remaining \(1\%\) volume is made up of several minor and trace constituents which include argon (Ar), carbon dioxide (\(\text{CO}_2\)), neon (Ne), helium (He), methane (\(\text{CH}_4\)), hydrogen (\(\text{H}_2\)), water vapor (\(\text{H}_2\text{O}\)), ozone (\(\text{O}_3\)), oxides of nitrogen (\(\text{NO}, \text{NO}_2\)), carbon monoxide (\(\text{CO}\)), hydrogen sulfide (\(\text{H}_2\text{S}\)), ammonia (\(\text{NH}_3\)) etc. found in infinitesimal amounts (parts per million (ppm) to parts per trillion (ppt) by volume), and suspended particulate matter (aerosols), which are widely variable in space and time. Despite being in small amounts aerosols play very important and crucial roles in the physico-chemical properties of the atmosphere, and the Earth-atmosphere radiation balance.

The Earth’s atmosphere shows significant and distinct variations in temperature as a function of altitude. The atmosphere is generally classified on the basis of atmospheric composition and temperature gradient. The Earth’s atmosphere from the surface to 100 km is called as the homosphere where all the constituents are well mixed, and above the homosphere lies the heterosphere wherein constituents (gases) are fractionated according to their molecular weight. The atmosphere characterised by the temperature gradient is divided into various horizontal layers as troposphere, stratosphere, mesosphere, and thermosphere (Figure 1.1). The transition altitudes distinguishing these layers are called tropopause, stratopause, and mesopause respectively. Tro-
The troposphere is the lowest layer of the Earth's atmosphere and extends from the Earth's surface upto 15-18 km in the tropics (Figure 1.1), and 8-10 km in the poles. Temperature decreases with altitude at the rate of 6.5°C per km in the troposphere (wet adiabatic lapse rate) and is characterized by strong convective mixing (Figure 1.1). Above the troposphere lies the stratosphere. The temperature increases with altitude (Figure 1.1) due to the significant absorption of ultra-violet (UV) component of the solar radiation by the ozone in the stratosphere. Troposphere and stratosphere account for more than 99.9%
of the mass of the atmosphere. Above the stratosphere lies the mesosphere, where the temperature decreases with altitude (Figure 1.1) and rapid vertical mixing takes place. The region above the mesopause is the thermosphere where temperature increases with altitude due to the absorption of solar radiation by atomic oxygen.

![Diagram of the Atmospheric Layers](image)

**Figure 1.2:** Schematic of the diurnal variation of Atmospheric Boundary Layer (based on Stull, 1988).

In the troposphere, the lowest part of the atmospheric layer which is strongly influenced by the Earth’s surface is called the atmospheric boundary layer (ABL) or planetary boundary layer, which holds most of the atmospheric constituents produced (natural and anthropogenic) at the Earth’s surface. The atmospheric layer extending from the top of the ABL to the tropopause is referred as free troposphere. ABL acts as a buffer which couples the Earth’s surface with the lower troposphere, and is directly influenced by the incoming solar energy. ABL evolves with the diurnal solar cycle (Figure 1.2). The height of the ABL exhibits significant spatio-temporal variation (ranging from few meters (stable conditions) to several kilometers (convective conditions)). ABL during day time is characterised by strong convection (convective mixed layer) and becomes turbulent due to the diurnal variation of the temperature and
shearing force (due to Earth’s surface friction on the surface wind). Turbulence in the convective mixed layer results in an effective dilution, and transport of the surface emitted pollutants. The convective mixed layer is capped by temperature inversion layer called as entrainment zone which confines pollutants and inhibits mixing below it. Entrainment zone isolates the ABL from the free troposphere. After sunset the air turbulence decreases due to radiative cooling which results in the formation of inversion layer (nocturnal layer) near the Earth’s surface (Figure 1.2). A non-turbulent residual layer forms above the stable nocturnal layer. During night time the emitted pollutants can remain trapped within the stable nocturnal layer. The heating of the Earth’s surface starts after sunrise which results in the mixing of the accumulated pollutants within the nocturnal layer with the convective mixed layer. The ABL dynamics plays an important and significant role in the diurnal distribution of the surface emitted pollutants (Seinfeld and Pandis, 1998).

1.1 Atmospheric aerosols

The particles (solid or liquid) suspended in air with radii range from 0.001 to 100 \(\mu\)m are called as atmospheric aerosols. They exhibit variability in shape, size, concentration and composition depending on the strength and nature of sources, production mechanisms, mixing characteristics, and scavenging processes. Aerosols of different sizes, magnitude and composition are produced by natural and anthropogenic sources, and can be transported to different regions depending on favorable meteorological (winds) conditions. Aerosols play a vital role in various atmospheric processes such as visibility, air pollution, cloud formation, radiation balance, atmospheric electricity, etc. Aerosol size is a crucial parameter that determines its interaction with the solar and terrestrial radiation, affects the physical and chemical properties, and their lifetime. Typically, the size (radius) of atmospheric aerosols span over five orders of magnitude, and based on their sizes and production mechanisms, the atmospheric aerosols can be classified as (i) nucleation mode (0.001 to 0.1 \(\mu\)m), (ii) accumulation mode (0.1 to 1.0 \(\mu\)m), and (iii) coarse (particles radii > 1.0 \(\mu\)m)
1.2 Sources, sinks and residence times of aerosols

Depending on the production sources, aerosols are classified as natural (e.g. sea salt, dust) and anthropogenic (e.g. black carbon). Typically, natural aerosols contribute \( \sim 80\% \) of the total aerosol in mass in the atmosphere.
Aerosols which are directly injected into the atmosphere are known as primary aerosols (e.g. wind blown dust, pollen grains, sea salt, black carbon from incomplete combustion of fossil fuel or biomass burning). There are several inorganic species in the atmosphere (sulfates, nitrates etc.) which are produced from the gas-to-particle conversion mechanism and these are known as secondary aerosols. Aerosols in the size range < 1.0 \( \mu m \) are mostly produced through condensation (gas-to-particle conversion) and coagulation processes (Figure 1.4), whereas particles > 1.0 \( \mu m \) are emitted directly by mechanical processes such as wind blown dust, sea spray, etc. (Figure 1.4). The coagulation is the process by which aerosols undergo random collisions and

Figure 1.4: Schematic of size distribution of aerosols (based on Whitby, 1978).
coalesce which results in a decrease in smaller size aerosols. The rate of coagulation is a function of mobility and the number density of aerosols (Warneck, 1988). Aerosols in the accumulation mode are produced either by coagulation of nucleation mode aerosols or by heterogeneous condensation of gaseous vapor onto smaller nucleation mode particles (Figure 1.4). Typically, the chemical nature of aerosols is mainly governed by their production source while their size distribution depends on their production mechanism. Mostly (> 99%) these aerosols are found in the atmosphere from the surface up to 40 km. The frequency of occurrence of aerosols from extraterrestrial sources (planetary accretion, comet debris and meteor shower) in the upper atmosphere (> 50 km) is rare and contribute < 1% in the atmosphere (d’Almeida et al., 1991).

The number concentration of the atmospheric aerosols exhibits large spatio-temporal variations. High number concentration of particles are found near to sources and their concentration decreases with distance from sources. Typically, the total aerosol number concentration over an urban and a rural region is found to be \( \sim 10^6 \) and \( 10^3 \) \( cm^{-3} \) respectively (Heintzenberg, 1997). In general, the total particle number concentration in the lower troposphere varies in the range of about \( 10^2 \) to \( 10^5 \) \( cm^{-3} \), and the concentration in the free troposphere is typically 1-2 orders of magnitude lower than lower troposphere (Heintzenberg, 1997). Aerosols in the stratosphere are significantly less in number (few to tens of particles). Stratospheric aerosols are produced by the diffusion of natural gases (like hydrogen sulfide, carbonyl sulfide, carbon disulfide, sulfur dioxide, etc.) from the troposphere. The number concentration of stratospheric aerosols increases significantly after a major volcanic eruption (Ramachandran et al., 2000).

Aerosols in the nucleation mode are primarily lost by coagulation processes. Although coagulation decreases the aerosol number concentration but the total volume remains constant. In the condensation process the aerosol number concentration remains constant but the total particle volume increases. When both (condensation and coagulation) processes exist
then aerosol number concentration decreases and the total aerosol volume increases (Seinfeld and Pandis, 1998). Nucleation mode aerosols undergo higher rate of condensation growth and coagulation, resulting in their transformation into accumulation mode aerosols. Atmospheric aerosols are removed from the atmosphere by dry and wet deposition processes. The removal of atmospheric aerosols vary as function of aerosol sizes, types, their residence times and altitude. Dry deposition refers to the removal of aerosols from the atmosphere to the Earth’s surface. It includes gravitational settling and impaction, and diffusion of particles to surface, which are active near the Earth’s surface. Wet removal of aerosols involves two processes, namely, below-cloud scavenging and in-cloud scavenging (Seinfeld and Pandis, 1998). The capture and removal of aerosol by the falling hydrometeors (rain, snow, cloud and fog drops) are called below cloud scavenging processes. In-cloud processes consist of activation of aerosols into cloud condensation nuclei, attachment of aerosols to the pre-existing cloud drops, and removal of aerosol containing cloud droplets produced by the first two processes by large falling hydrometeors. Aerosols found in the size range of 0.1-10 µm are mainly removed by wet deposition, and for aerosols > 10 µm sedimentation is the dominant removal process (Jaenicke, 1993).

The time spent by the aerosols in the atmosphere from their production to removal or conversion can be referred to as residence time of atmospheric aerosols. It depends on their size, chemical composition, phase (solid or liquid), morphology and altitude at which they are present. Nucleation mode aerosols are removed efficiently by coagulation processes, and hence, their residence time is very short. The residence time for coarse mode (> 10 µm) aerosols is also short in the atmosphere due to sedimentation (gravitational settling) (Figure 1.5). The residence time of atmospheric aerosols in the accumulation mode is the longest (~ 7-10 days), because the coagulation and sedimentation processes are least significant in this size range. The aerosols in the accumulation mode is removed predominantly from the atmosphere by wet deposition processes (Figure 1.5). The residence time of aerosol types also
vary; sulfate, sea salt, dust and black carbon aerosols have a residence time on the order of 2-7 days (Textor et al., 2006). The residence time is of the order of few days within the atmospheric boundary layer, few weeks in free troposphere and few years in the stratosphere (Jaenicke, 1993) (Figure 1.5).

1.3 Significance of atmospheric aerosols

Aerosols have the potential to significantly influence our planet by interacting with incoming solar (shortwave) and outgoing terrestrial (longwave) radiations through three distinct radiative effects, viz. (i) direct effect, (ii) semi-direct effect, and (iii) indirect effect (IPCC, 2007). The quantification of the effect of
a species in modifying the balance between the incoming and outgoing flux in the Earth-atmosphere system is defined as radiative forcing of the species (IPCC, 2013). Positive and negative radiative forcing indicate the warming and cooling the Earth-atmosphere system respectively. The direct radiative effect of aerosols involve scattering and absorption of solar and terrestrial radiation in the atmosphere (IPCC, 2007). Both these processes reduce the direct solar flux reaching the Earth’s surface and thus induce a net cooling effect on the surface (negative forcing). In the shortwave region, a scattering aerosol (e.g., sulfate) will cool the atmosphere, while an absorbing aerosol (e.g., black carbon) will warm the atmosphere. Absorption of solar radiation by aerosols leads to heating of the air, which can result in an evaporation of cloud droplets which is referred to as semi-direct effect. Semi-direct effect is a consequence of the direct effect of absorbing aerosols and may have a significant warming impact on climate by ’burning off’ of the low clouds that scatter solar radiation back to space but have little impact on outgoing longwave radiation. Indirect radiative forcing by aerosol is the overall process by which aerosols perturb the Earth-atmosphere radiation balance by modulating the cloud albedo and amount (IPCC, 2013). Aerosol plays an important and significant role in the formation of clouds, and serves as cloud condensation nuclei around which cloud droplets are formed. Higher aerosol concentration can increase the formation of smaller droplets with decreased droplet radius, which leads to an increase in cloud albedo and hence leads to a cooling effect known as Twomey effect (Twomey, 1977). The aerosol radiative forcing in the longwave regime contributes about 10% to the net aerosol radiative forcing. This contribution is much smaller than the contribution of shortwave aerosol radiative forcing to the net forcing (Ramanathan et al., 2001a; Ganguly et al., 2005; Ramachandran et al., 2006).

Aerosol properties (optical, physical and chemical) exhibit large spatial and temporal variability, hence the radiative effects of aerosol can be different in contrast to greenhouse gases. Aerosol plays a significant role in the Earth’s radiation budget and is a large source of uncertainty in the predic-
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tion of climate change (IPCC, 2013). The major sources that contribute to the uncertainty on aerosols and their radiative forcing are, uncertainties in their properties (optical, physical, and chemical), uncertainties/assumptions involved in the estimates of radiative forcing, and inaccuracy in their atmospheric burden and the anthropogenic contribution (IPCC, 2013). The inaccuracies in aerosol properties arise from uncertainties in its size distribution, chemical composition, and meteorological effects. In order to increase the level of scientific understanding, it is necessary to have spatial and high temporal resolution measurement of various aerosol properties. There exists a large uncertainty in the forcing due to different aerosol species because of significant uncertainty in their sources (natural and anthropogenic), and their spatio-temporal variations (Ramachandran et al., 2012). Further, of the various aerosol species the black carbon aerosol (anthropogenic source) is the second largest source to global warming, after carbon dioxide ($CO_2$) (Ramanathan and Carmichael, 2008) and hence, the estimation of radiative forcing due to black carbon aerosol is important to delineate/determine the anthropogenic contribution with respect to the total (composite) radiative forcing.

Black carbon (BC) aerosol is the optically absorbing component of carbonaceous aerosols and is produced by incomplete combustion of fossil fuel (coal, diesel, petrol, etc.), biofuel (biodiesel, biogas, ethanol, etc.) and biomass (woods, shrubs, dry leaves, etc.). It absorbs incoming shortwave solar radiation and outgoing longwave terrestrial radiation, and is therefore an important contributor to the direct radiative forcing through warming the atmosphere. It has a short lifetime (~ 7-10 days) in the atmosphere but exhibit significant spatial and temporal variability in its sources and emission. The physical (size distribution and morphology) and chemical (composition and mixing state) properties of the atmospheric BC aerosols are complex and variable in nature (Xianda et al., 2016). BC aerosol significantly affects the human health (respiratory and lung diseases, Mauderly and Chow (2008)), vegetation (crop yields, Chameides et al. (1999)), ecosystem (terrestrial and aquatic,
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Forbes et al. (2006), monsoon Wang et al. (2009), and glaciers (Lau et al., 2006; Li et al., 2016). The emissions from fossil fuel burning consists of large amount of black carbon aerosols as compared to organic carbon, whereas biomass (wood) burning consists dominantly organic carbon aerosols. Typically, black carbon and organic carbon aerosols are found to absorb in the near infrared and ultraviolet wavelengths respectively (Sandradewi et al., 2008). The black carbon aerosols produced from the combustion of fossil fuel and biomass are found to exhibit a largest uncertainty in aerosol emissions (Bond et al., 2004). A significant uncertainty in forcing arises because of the lack of information about the amount of BC aerosol emitted into the atmosphere, its size distribution, contribution from different sources (fossil fuel and biomass burning), and its mixing state. The relative contributions of BC mass from the combustion of fossil fuel and biomass to the total BC mass concentration are used to quantify the dominant source (fossil fuel or biomass) of BC aerosols. Due to the above there is a significant interest in studying the characteristics of black carbon aerosols and their radiative and climatic impact over different environments (e.g. urban (Ramachandran and Rajesh, 2007; Sreekanth et al., 2007; Beegum et al., 2009; Panicker et al., 2010; Ramachandran and Kedia, 2010; Wang et al., 2011; Dumka et al., 2013; Safai et al., 2013; Tiwari et al., 2013; Gong et al., 2016; Rajesh and Ramachandran, 2017), rural/semi-urban (Gadhavi and Jayaraman, 2010; Kumar et al., 2011; Aruna et al., 2013; Singh et al., 2015), ocean (Kedia et al., 2012; Kompalli et al., 2013), and mountain sites (Dumka et al., 2010; Raju et al., 2011; Kant et al., 2012; Srivastava et al., 2012; Panwar et al., 2013; Udayasoorian et al., 2014; Sarkar et al., 2015)).

1.4 Motivation

The Indian subcontinent and its surrounding regions are the prime sources for different types of aerosols (natural and anthropogenic origin) such as mineral dust, black carbon, sea salt, sulfate, etc., and in addition, the subcontinent experiences tropical climatic conditions which results in significant variations in temperature, relative humidity and rainfall on seasonal time scales.
Hence, large spatio-temporal variabilities have been observed in aerosol characteristics over India. The study on the influence of aerosols from natural and anthropogenic sources on radiative effects has been undertaken over different environments in Indian subcontinent and adjoining oceanic regions (e.g., Ramanathan et al. (2001b); Jayaraman et al. (2006); Ganguly et al. (2006); Ramachandran and Cherian (2008); Kedia et al. (2010); Pathak et al. (2010); Ramachandran and Kedia (2012); Jose et al. (2016); Sharma et al. (2017); Verma et al. (2017); Srivastava et al. (2018)). But, aerosols are still a significant source of uncertainty in climate change prediction because of limited information of aerosol characteristics on temporal and regional scales. The measurements of aerosol characteristics and their radiative effects over India (Pandithurai et al., 2004; Niranjan et al., 2005; Jayaraman et al., 2006; Ramachandran et al., 2006; Sreekanth et al., 2007) and over oceans surrounding peninsular India (Jayaraman et al., 1998; Ramanathan et al., 2001b; Ramachandran, 2005; Kedia and Ramachandran, 2009, 2011) have been extensively reported, but relatively a few measurements exist over western India (Ganguly and Jayaraman, 2006; Ramachandran and Rajesh, 2007; Ramachandran and Kedia, 2010). The western India is densely populated, and is surrounded by desert (Thar), ocean (Arabian Sea) and large land mass with different aerosol species produced and transported from different regions. Also, studies documenting the contribution of fossil fuel and biomass burning (wood burning) to total BC are scarce. In addition, investigation on the simultaneous measurements of BC characteristics over a source region, and a nearby background region are not available, which is required to simulate better the seasonal BC aerosol distribution in regional and global models, and estimate their radiative effects more accurately.

The present study focuses on the space-time characteristics of optical and physical properties of aerosols, source apportionment of black carbon aerosols, and their radiative effects over an urban, and a high altitude remote region. Typically, urban emissions are influenced by anthropogenic activities. The high altitude remote region is influenced by local and longrange transported aerosols through convective and advective processes. When the
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high altitude remote location is in the same region as that of an urban aerosol source region, and is governed by the same meteorology and atmospheric dynamics, then aerosol measurements over the high altitude region can serve as regional representative background.

### 1.5 Objectives

With an objective to investigate the spatio-temporal variations in aerosol properties over western India, for the first time, simultaneous measurements of various aerosol properties were conducted over distinct environments (urban, and high altitude remote) for the scientific reasons mentioned above.

The specific objectives of the present thesis are:

1. *To characterize the spatial and temporal variabilities in optical and physical properties of aerosols over urban, and high altitude remote locations.*

2. *To characterize the spatial and temporal variabilities in black carbon aerosol, and its source apportionment over urban, and high altitude remote locations.*

3. *To estimate the total direct aerosol radiative forcing and the radiative forcing due to black carbon aerosols only, and their seasonal variability over urban, and high altitude remote regions using the aerosol optical and physical characteristics.*

Aerosol characteristics were measured and analysed over an urban environment (characterized by highest aerosol concentrations dominated by anthropogenic aerosols) (Ahmedabad (23.03°N, 72.55°E, 55 m above mean sea level), and a high altitude remote region (with low aerosol concentration dominated by transport mechanisms) (Gurushikhar (24.65°N, 72.78°E, 1680 m above mean sea level) over western India. Further, utilising the measured aerosol characteristics and models, radiative forcing for composite and BC
aerosols are estimated and discussed.

The thesis consists of six chapters. The present chapter (Chapter 1) gives a brief introduction to the Earth's atmosphere, atmospheric aerosols, their sources and sinks in the atmosphere, size distribution and their composition. It consists of a brief description on how the aerosols perturb the Earth-atmosphere radiation budget. In addition, this chapter consists a brief review of the previous research in India, thus, setting the stage for the motivation, objectives and importance of the thesis. Chapter 2 provides a brief description of the various instruments used in the study along with their measurement techniques. Methodology, and data analysis are discussed in this chapter. It also consists a description about the satellite data obtained from different sensors which are used in the present study. The uncertainties involved in various measurements are also discussed in this chapter. A brief description of various computational tools used for radiative transfer estimation, namely, Optical Properties of Aerosols and Clouds (OPAC) (Hess et al., 1998), and Santa Barbara DISORT Atmospheric Radiative Transfer (SBDART) (Ricchiazzi et al., 1998) are also included. Chapter 3 discusses the measured optical and physical properties of aerosols over the study locations in western India. Chapter 4 deals with the spatial and temporal characteristics of black carbon aerosol and its source apportionment over an urban and a high altitude remote locations. Chapter 5 discusses the seasonal variabilities in the radiative forcing over urban and high altitude remote locations in western India. In order to quantify the effect of BC aerosols on the radiation budget the aerosol radiative forcing is estimated for composite and BC aerosols, and discussed. Chapter 6 summarises the major results from the study and discusses the scope for future work.