CHARACTERIZATION, PROPERTIES AND CLIMATIC IMPLICATIONS OF AEROSOLS IN NORTHERN PAKISTAN

By

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This dissertation of Mr. Bahadar Zeb submitted for the Degree of Doctor of Philosophy with a major in Physics and titled “CHARACTERIZATION, PROPERTIES AND CLIMATIC IMPLICATIONS OF AEROSOLS IN NORTHERN PAKISTAN” has been reviewed in final form. Permission, as indicated by the signatures given below, is now granted to submit the copies to University of Malakand for the final evaluation process.

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Abstract

The microphysical, chemical and optical properties of atmospheric aerosols were studied during the different study periods from 2004-2016 over Peshawar, Glaciated areas (Astore, Gilgit, Sost and Skardu) and Dir (Upper) Pakistan. Moreover, the air quality and climatic implications of aerosols were also studied over these locations.

Particulate Matter (PM) plays a vital role in altering air quality, human health and climate change. There are sparse data relevant to PM characteristics in urban environments of the Middle East, including Peshawar city in Pakistan. This work reports on the morphology and composition of PM in two size fractions (PM$_{2.5}$ and PM$_{10}$) during November 2016 in Peshawar. The 24 hours mass concentration of PM$_{2.5}$ varied from 72 µg/m$^3$ to 500 µg/m$^3$ (average 286 µg/m$^3$) and that of PM$_{10}$ from 300 µg/m$^3$ to 1440 µg/m$^3$ (average 638 µg/m$^3$).

The morphology, size and elemental composition of PM were measured using Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) Spectroscopy. The major identified sources of PM are vehicular emissions, biomass burning, soil and re-suspended road dust, biological emissions and construction activities in and around the vicinity of the sampling site.

Glacier melting due to light-absorbing aerosol has become a growing apprehension in recent decades. The emphasis of this study is to examine absorbing aerosol loading over the high mountain glacier region of northern Pakistan covering a long term of twelve years (2004 – 2016), with sources including local emissions and long-range transported pollution. Optical properties of aerosols were seasonally analyzed over the glacier region (35-36.5°N; 74.5-77.5°E) along with three selected sites (Gilgit, Skardu and Diamer). The highest values of aerosol optical depth (AOD) and single scattering albedo (SSA) occurred during spring, whereas aerosol index (AI) and absorption AOD (AAOD) exhibited maximum values in winter and summer. The value of AOD decreases in winter and that of AI decreases in
autumn. Similarly, the value of AAOD decreases in winter and that of SSA in autumn. The results revealed that in spring and summer the prominent absorbing aerosols were dust whereas in autumn and winter mixed anthropogenic aerosols were prominent. Maximum values of radiative forcing within the Atmosphere (ATM) were observed during the summer, followed by spring, autumn and winter. Trend analysis shows that AI, AOD and AAOD increased at the rate of 0.005, 0.006 and 0.0001 yr\(^{-1}\), respectively, while SSA decreased at the rate of 0.0002 yr\(^{-1}\). With the time, the melting of ice gets accelerated which is suggestive of absorbing aerosol types in the region. CALIPSO data indicate that the regional aerosol was mostly comprised of sub-types categorized as dust, polluted dust, smoke and clean continental. The analysis of the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model revealed that the air parcels were arriving to glacier region from different source sites.

Over the high-altitude Himalayan regions in South Asia, absorbing aerosols, particularly black carbon (BC) and dust, have strong effects on the hydrological cycle and climate. This study reports on BC aerosol measurements during May, June, November and December (2016) over Astore, Gilgit, Sost and Skardu (northern Pakistan). Diurnal and monthly variations of BC aerosol were examined in relation to meteorology. BC aerosols exhibited diurnal variations with sharp morning and evening peaks associated with local anthropogenic aerosols in addition to long-range transport. During May, the BC concentrations were in the range of 2.3 – 2.9 µg/m\(^3\), 2.1 – 4.7 µg/m\(^3\) and 0.9 – 1.6 µg/m\(^3\) in Astore, Gilgit and Sost, respectively. During June at Skardu, BC was found in the range from 2.6 – 4.1 µg/m\(^3\). During November at Astore and Gilgit, BC varied from 2.5 – 3.7 µg/m\(^3\) and from 3.5 – 4.7 µg/m\(^3\), respectively. During December at Gilgit, Sost and Skardu, BC concentrations varied from 2.8 – 6.1 µg/m\(^3\), 1.5 – 2.7 µg/m\(^3\) and 3.2 – 4.7 µg/m\(^3\), respectively. BC aerosols exhibited positive correlations with temperature and wind speed, in addition to a negative correlation
with relative humidity. The long-range transport of aerosols to the receptor sites were found to be from central Asia, Eastern Europe, Middle East and India as well.

At Astore, Gilgit, Sost and Skardu, the Aerosol Radiative Forcing due to Black Carbon were calculated at TOA, SRF and within ATM during the month of May, June, November and December (2016). BC number density corresponding to BC mass concentration was used in OPAC model for the estimation of aerosols optical properties. The model derived optical properties along with atmospheric parameters were used in SBDART model for the calculation of BC radiative forcing at the TOA, SRF and within ATM. For the entire study period, the surface reflectance varied from 0.09 (17 Nov) at Astore to 0.42 (23 Dec) at Skardu with an average value of 0.21 ± 0.08 over four locations. Daily columnar ozone varied from minimum value of 23 ppb at Sost on 13 December to maximum value of 55.27 ppb at Skardu on 3 June with an average of 36.86 ± 9.6 ppb. Similarly, columnar water ranged from 0.06 cm on 23 May to 0.78 cm on 11 May at Gilgit with an average value of 0.33 ± 0.14. The lowest and highest BC concentration of 0.75 µg/m³ and 6.06 µg/m³ with corresponding modeled derived AOD of 0.19 and 0.25 was found on 2 June and 1 December at Skardu and Gilgit, respectively. Likewise, SSA and AP range from 0.78 (Gilgit) to 0.95 (Skardu) and from 0.68 (Gilgit) to 0.71 (Skardu), respectively. BC radiative forcing at the TOA ranged from minimum value of -0.07 W/m² at Sost on 16 December to maximum value of 13.92 W/m² at Skardu on 3 June, while at SRF it ranged from -7.31 W/m² on 2 June at Skardu to -54.41 W/m² on 1 December at Gilgit. Similarly, BC radiative forcing within ATM varied from 10.14 W/m² (2 June) to 48.92 W/m² (1 December) with corresponding heating rate of 0.28 K/day to 1.37 K/day on the above dates at Skardu and Gilgit, respectively.

The study of the optical properties of aerosols over Dir (Upper), a high latitude place of North Pakistan) were carried out from 2004 to 2016 to understand the aerosol loading and its variability. The maximum average AOD value of 0.30 ± 0.05 was found in July while
maximum AE value of 1.17 ± 0.09 was noted in December. Similarly, the minimum AOD (0.09 ± 0.04) was found in December whereas minimum value of AE (0.51 ± 0.07) in May. The maximum average seasonal AOD (0.28 ± 0.05) and AE (1.030 ± 0.07) was investigated in summer and winter season, respectively. Likewise, the minimum AOD (0.12 ± 0.05) was observed in winter and minimum AE (0.56 ± 0.04) in spring season. Seven-days back trajectories were computed, which shows that the air mass (500 m) reaching the study region during four seasons. Different transported particles were suggested during different seasons.

To understand the effects of PM on human health and climate is of great importance. The morphological and chemical characterization of PM has attained significant importance in the recent years, because such data are needed to accurately constrain aerosol radiative properties and health impacts. Particulate Matter like, PM$_{10}$, PM$_{2.5}$ and ultra-fine aerosols have different characteristics, sources and potential health effects. Particularly the fine PM fraction can more easily penetrate into the lungs and cause respiratory diseases. BC aerosol can damage the cells of the human body and lead to cancer. The forcing implications over the glacier region are very crucial for climate modelling tasks and adaptation to the potential effects of the change in melting rates of ice. As BC aerosols have an important role on the melting of Himalayan glaciers and on radiative forcing, therefore its study over high-altitude sites at Himalaya has a special importance. The information about BC over these high altitude locations is very helpful for the understanding of local and regional weather and climate change.

The current research work will motivate the researchers to make new and efficient instruments for the constant monitoring of atmospheric aerosols. This work will also motivate the researchers to prepare high quality filters which collect PM excellently and identify each element in PM.
Acknowledgements

To complete this Dissertation is an uphill task, but Allah almighty made this task easy for me and today with the blessing of Allah almighty I have completed this Dissertation. I am very thankful to my supervisors Prof. Dr. Iftikhar Ahmad and Dr. Khan Alam who guided me by his propound knowledge and experience in this research work and providing me the best facilities related to my research work. I am frankly accepted that without their active support, advice and guidance the present research task was not possible. I wish to offer my heartiest thanks to my research colleague Humera Bibi, Samina Bibi, Maryam Fahim, Maqbool Ahmad at the department of physics university of Peshawar for their step-by-step guidance on various stages of my PhD study. I am extremely grateful to my parents, brothers and sisters for their love, patience and support throughout my PhD studies. Special thanks to my wives for her moral support during the process of the completion of my PhD.

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Bahadar Zeb
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This thesis consists of the following published paper

DEDICATION

FOR

MY

PARENTS, BROTHERS, WIVES AND KIDS
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<td>AAOD</td>
<td>Absorption Aerosol Optical Depth</td>
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<tr>
<td>AE</td>
<td>Angstrom Exponent</td>
</tr>
<tr>
<td>AERONET</td>
<td>Aerosol Robotic Network</td>
</tr>
<tr>
<td>AI</td>
<td>Aerosol Index</td>
</tr>
<tr>
<td>AMSL</td>
<td>Above Mean Sea level</td>
</tr>
<tr>
<td>AOD</td>
<td>Aerosol Optical Depth</td>
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<tr>
<td>AP</td>
<td>Asymmetry Parameter</td>
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<td>ARF</td>
<td>Aerosol Radiative Forcing</td>
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<td>ATM</td>
<td>Atmosphere</td>
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<tr>
<td>AVG</td>
<td>Average</td>
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<tr>
<td>BC</td>
<td>Black Carbon</td>
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<td>CALIPSO</td>
<td>Cloud- Aerosol Lidar and Infrared Pathfinder Satellite Observations</td>
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<td>CERES</td>
<td>Clouds and the Earth’s Radiant Energy System</td>
</tr>
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<td>DB</td>
<td>Deep Blue</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental Carbon</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-Red</td>
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<tr>
<td>HR</td>
<td>Heating Rate</td>
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<tr>
<td>HYSPLIT</td>
<td>Hybrid Single Particle Lagrangian Integrated Trajectory</td>
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<tr>
<td>IGP</td>
<td>Indo Gangetic Plain</td>
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<tr>
<td>MODIS</td>
<td>Moderate Resolution Imaging Spectroradiometer</td>
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<tr>
<td>OC</td>
<td>Organic Carbon</td>
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<tr>
<td>OMI</td>
<td>Ozone Monitoring Instrument</td>
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<tr>
<td>OPAC</td>
<td>Optical Properties of Aerosols and Clouds</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-----------------------------------------------</td>
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<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>RF</td>
<td>Rain Fall</td>
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<td>RH</td>
<td>Relative Humidity</td>
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<td>SBDART</td>
<td>Santa Barbara DISORT Atmospheric Radiative Transfer</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SRF</td>
<td>Surface</td>
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<td>Single Scattering Albedo</td>
</tr>
<tr>
<td>Temp</td>
<td>Temperature</td>
</tr>
<tr>
<td>TOA</td>
<td>Top of Atmosphere</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VDR</td>
<td>Volume depolarization ratio</td>
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<tr>
<td>WD</td>
<td>Wind Direction</td>
</tr>
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<td>WS</td>
<td>Wind Speed</td>
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Introduction

1.1 Atmospheric Aerosols

Aerosols are minute solid or liquid particles or their mixture up in the atmosphere [1]. The various types of aerosols include smoke, fog, smog, fume, mist, clouds and haze etc. [2]. Aerosols possess great difference in their nature, size, emission sources and optical properties and are the important part of the earth-ocean-atmosphere system. The diameter of aerosols normally ranges from a few nanometres to several of micrometres and strongly depends on formation mechanism, sources and age of the particles [2]. Aerosols have small existence period i.e. from few hour to days. Due to the smaller size, aerosol presence is high in the atmosphere and can be migrated over long distance [3]. The primary sources of aerosols are those from which particles are emitted directly and secondary sources are those from which particles are produce due to chemical reactions. The sources of the aerosol formation are either natural or anthropogenic in term of primary and secondary aerosols. The primary aerosols generated from natural sources are volcanic emission, sea salt, dust, forest burning etc. Likewise the primary aerosol produce from anthropogenic sources include industrial emission, petroleum refineries, combustion of fossil fuel, indoor cooking, biomass burning, vehicular emission etc. Similarly secondary aerosols are mainly generated in the atmosphere through various mechanisms [4].

1.2 Aerosols Classification

There are several ways in which the aerosols can be categorized. One of the primary categories is size. In general, particles below 2 – 2.5 µm are called fine particles. Similarly particles greater than 2.5 µm are named coarse aerosol particles. Usually, the coarse particles are created naturally e.g., wind-blown dust and sea sprays whereas fine mode aerosols
produce by anthropogenic activities i.e. Black Carbon (BC), organic aerosol, nitrate, sulfates etc. The fine particles are usually produced from a series of processes often involving chemical changes. Therefore, the fine particle category is further separated into ultra-fine, nuclei or Aitken and accumulation size particles. The ultra-fine particles are the smallest particles, usually only a few nanometers in size and are created by gas to particle exchange of the lower volatility gases. The nuclei particles range from approximately 10 nm to 80 nm and usually produce from condensation of low volatility gases. Accumulation particles, ranging between 80 nm and 1-2 μm, usually produce from coagulation of smaller particles and also from condensation process [4, 5]. The aerosol diameter lies in the range from 0.05 to 10 μm are of utmost interest for many applications because in this range the aerosol direct interaction with sunlight is dominant, and also make up the majority of the aerosol masses. The aerosol particles have different shapes like platelets, isometric and fibres, but its spherical shape is considered for convenience [2]. The analysis of the particle size distributions is very important, because due to this distribution the anthropogenic and natural aerosols can be distinguished [6].

Aerosols can be divided into absorbing and scattering types on the basis of radiations absorption or scattering. Absorbing aerosols include BC, some organic carbon and dust while scattering components includes sea salt, nitrate and sulphate etc. [7]. Absorbing aerosols absorb light and at last tends to produce warming effect, while scattering types of aerosols scatter light back to space and hence cause cooling effects.

1.3 Life Time and Removal Mechanism of Aerosols

Different factors (formations, coagulation and transformations) affects the life period of atmospheric aerosols. Generally, in stratosphere the life time of aerosols is greater (up to two years) than troposphere (up to week or month). Small size aerosol particles can stay in lower troposphere for about a week but its life time increases with increasing altitudes. Larger size
aerosol particles have shorter life time in atmosphere due to greater settling velocity. Atmospheric aerosols removes with dry deposition like gravitational settling, turbulent deposition and through wet depositions i.e. washout, rainout and scavenging process as shown in Figure 1.1. Due to these mechanisms, the coarser particles are removed very effectively. Similarly fine particles can be removed when they develop to a bigger size through different process (coagulation, condensation and cloud formation).

Figure 1.1: Cycling of atmospheric aerosol particles [8].

1.4 Aerosols over the Study Region

(a) Aerosols over (Himalaya-Karakorum-Hindu Kush) Region

Over the Indian sub-continent strong anthropogenic emissions cause to the development of thick layers of aerosols, which can be migrated to the great height locations of the Himalaya-Karakorum-Hindu-Kush (HKH) region. A large portion of aerosol contains significant amount of light absorbing particles e.g. BC, Organic Compounds (OC) and dust. These absorbing particles, apart from greenhouse gases can contribute to warming effects in the atmosphere. Srivastava et al. [9] reported that the Himalaya region work as a strong wall to the aerosol pollutants, comprising dust transported by westerly wind and stacked against the slope of the
hills, thus rising dust concentration in the foothill of Himalayan range. Lau and Kim [10] proposed that in the prominent region of HKH the absorbing types of aerosols cause much rise in the precipitation.

The transportation of aerosol to the Himalayan region is an important mechanism, because it improves the explanation of the impacts of BC on Indian Summer Monsoon precipitation and on the storage of frozen water in the HKH regions. BC aerosols also deposits on the snow exterior, reducing the reflectance, thus changing its energy budget [11, 12]. Over some part of the high Himalayan region, Flanner et al. [11] reported that due to the existence of BC aerosols, the radiative forcing reached to 20 W/m², which confirmed that in carbon climate forcing, the snow darkening play an important role. As a result of snow darkening the melting process increasing rapidly. The most recent observation over Himalayan region indicates the problem of the influence of optically active material on the local energy budget. These observations indicate that mountain breezes cause various aerosols transported up to the high altitude regions from India and Pakistan [13-17]. Over Nepal Himalaya, Carrico et al. [13] investigated that aerosols build up at the start of the spring and during the winter season, with comparatively great quantity of radiations absorbing aerosols. Huang et al. [18] investigated new mechanism of the transportation of aerosols from the sources of pollutions to Tibetan and Himalayan locations. Dumka et al. [19] investigated that over Himalayan region the aerosols transported upward and results to change in solar irradiance. Figure 1.2 represents the mechanism by which aerosols transported from lower areas to high altitude regions.
(b) Aerosol over Urban Regions

Numerous activities in urban environments generate large amounts of primary aerosols. Due to its high pollution emission and dense population, the urban locations have become the major sources of aerosols (natural and anthropogenic) and their precursor gases. In urban locations the anthropogenic sources of aerosols are dominated by natural sources and its mass concentration varied from a few tens of $\mu g/m^3$ to a single value $mg/m^3$. The major sources of aerosols in urban areas included industrial activities, construction activities, petrol and diesel engines, which produce carbonaceous aerosols and road dusts. Urban aerosols produce health problems [21] and also cause loss of visibility and affects air quality [5]. At present, the industrial emission in urban regions cause fog and smog that are frequently associated to coal burning and traffic as well. The meteorological situations and seasonal variations in urban locations have an influence on the emission of aerosol particles. In urban atmospheric environment different photochemical reactions during spring and summer seasons produce gases and successive nucleation [22, 23]. Therefore, it is very important to know the nature of
urban aerosols and precursor gases, because they affect human health, climate, weather and ecosystem.

**1.5 Black Carbon Aerosols**

In order to know the impacts of absorbing aerosols on the change of climate, its characterization is of great importance. BC and iron oxides in dust are the main absorbing kinds of atmospheric aerosols [24]. BC aerosols are produced due to the incomplete combustions of carbonaceous fuels like biomass, fossils fuels, agriculture and forest waste. It is one of the vital radiation absorbing constituent of atmospheric aerosols, developing into a collection of fine particles, which contribute to nearly 90% in PM$_{2.5}$ of airborne PM [25-28].

BC has been getting much attention because it strongly absorbs the solar radiations in shortwave region and hence plays a vital role in altering the earth climatic system [29]. After CO$_2$, BC is the greatest contributors to the global warming effects [30-32]. BC aerosols absorb incoming solar radiation, produce warming effects as compare to other aerosols like sulfates etc., that reflect light and hence producing cooling effects [33, 34]. BC aerosols absorb toxic substances because of its absorptive and porous nature and produce harmful health effect, contaminate construction materials, decrease crop yields and badly affect the global ecosystem [25, 35]. BC aerosol particles also change the snow and ice melting, reflectivity from snow surface, cloud life time and precipitation [32]. In the lower troposphere the life time of BC aerosols $\geq$1 week [36], therefore BC aerosols face the long-range transportation [26]. The most important removal process of BC aerosol particles are wet deposition because of its fine structure [37]. Because of its strong absorptive property, BC aerosols may decrease the surface reflectance and that is why in climate modelling its surface reflectance is considered to be among the highest radiative uncertainties.
1.6 Physical and Optical Properties of Aerosols

1.6.1 Scattering
Scattering is actually the re-direction of radiations strike on a particle. Due to scattering the electric charges inside the particles arrange themselves in one or more dipoles, as a result of which the particle re-radiates secondary spherical waves in all direction. The size of the aerosol shows a very central part in the angular distribution of the scattered radiations although the total energy remains constant [38]. During elastic scattering the waves (primary and secondary) have the similar frequency which is further divided into two criteria: Mie scattering and Rayleigh scattering. In this type of scattering different multi-poles are induced and the scattering arrangement turn into more complicated form. During Mie scattering the forward scattering becomes more important than backward scattering of radiation from aerosol particles. Similarly in Rayleigh scattering the wavelength of the radiations is greater than the particle size.

1.6.2 Absorption
When the incoming radiations are passing through a material, they losses their energy during its passage and hence increase their internal energy named absorption. The energy absorbed is re-emitted as thermal energy or at other wavelengths. A very common law called Lambert Beer Law, explains aerosols absorption and is given by the equation as:

\[ I = I_0 e^{-\alpha l c} \]  

(1.1)

where \( I \), \( I_0 \) represent outgoing, incident intensity of light and \( \alpha \), \( l \) and \( c \) denote absorption cross-section, the path length and the concentration, respectively [39]. Although the deep and informative study of the absorbing types of aerosols are very much important because this study gives information’s about the climatic change, the knowledge of absorption of light by aerosols is still uncertain.
1.6.3 Aerosol Optical Depth (AOD)
AOD represents the attenuated radiations by atmospheric aerosol through the process of
scattering or absorption. In other words, AOD shows that how much direct sunlight is not
permitted by the aerosol particle to reach the ground.

Mathematically AOD is given as

\[
AOD(\lambda) = \int_{h_1}^{h_2} \beta_{\text{ext},\lambda}(h) \, dh
\]

(1.2)

where \( \lambda \) and \( \beta_{\text{ext}} \) is the wavelength and extinction coefficient, respectively, and \( h_1 \) and \( h_2 \) is
lower and upper altitude in units of length, respectively. AOD is the key optical parameter,
which is used for the calculations of radiative forcing.

1.6.4 Ultraviolet Aerosol Index (UVAI)
UVAI referred to hereafter as AI and is very useful index. The AI is basically a quantification
of the change in the quantity of Rayleigh scattered light [40, 41].

It is very suitable parameter that measure UV absorbing aerosols [42]. AI can characterize
the absorbing types of aerosol, which focus on concentration, altitude and on the optical
properties of aerosols [43]. AI can detect smoke, volcanic ash and dust. Quantitatively for
Ozone Monitoring Instrument (OMI), AI can be expressed as

\[
AI = 100 \log_{10} \left[ \frac{I_{360-\text{means}}}{I_{360-\text{calc}}} \right]
\]

(1.3)

where \( I_{360-\text{means}} \) is the backscattered radiance and \( I_{360-\text{calc}} \) is the radiance calculated from the
model.

1.6.5 Absorption Aerosols Optical Depth (AAOD)
AAOD is the assessment of the concentration of near-UV absorbing aerosol [44]. We can
find out AAOD by using the following equation if the value of SSA and AOD are known:

\[
AAOD(\lambda) = [1-\text{SSA}(\lambda)] \, AOD(\lambda)
\]

(1.4)

where \( \lambda \) represents wavelength.
1.6.6 Single Scattering Albedo (SSA)
SSA gives quantitative details about absorption and scattering aerosols and can be used to find aerosol radiative forcing. Characteristics of aerosols (scattering, absorption and surface reflectance) provide knowledge about heating or cooling effects of aerosol [45]. SSA is the ratio of the scattering efficiency to the extinction efficiency of aerosols and is usually expressed by the following equation:

\[
SSA = \frac{Q_{\text{scat}}}{Q_{\text{ext}}} = \frac{Q_{\text{scat}}}{Q_{\text{scat}} + Q_{\text{abs}}}
\]  

(1.5)

where \( Q_{\text{scat}} \) represent scattering efficiency and \( Q_{\text{ext}} \) denote extinction efficiency i.e. \( Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{scat}} \). 0 value of SSA represents complete absorption while 1 value denotes complete scattering.

1.7 Aerosol Radiative Effects
Aerosol Radiative Forcing (ARF) at the Top of Atmosphere (TOA) or at the surface (SRF) is the difference between the incoming and outgoing solar fluxes with and without aerosols and is given by the equation as follows:

\[
\Delta F = (F_{\text{all} \downarrow} - F_{\text{all} \uparrow}) - (F_{\text{clr} \downarrow} - F_{\text{clr} \uparrow})
\]  

(1.6)

where \( \Delta F \) represents irradiance (incoming or outgoing solar flux) and \((F_{\downarrow} - F_{\uparrow})\) represents the net irradiance (incoming solar flux minus outgoing solar flux) computed in all sky \((F_{\text{all}})\) and clear sky \((F_{\text{clr}})\) either at the TOA or SRF [46]. The positive and negative value of radiative forcing indicates net warming and cooling effects, respectively. The change in ARF at the TOA and at SRF in the presence and absence of aerosols gives radiative forcing within atmosphere (ATM), which denotes the quantity of energy absorbed by atmospheric aerosols and converted into heat.

1.8 Atmospheric Heating Rate (HR)
HR can be determined by the equation as
\[
\frac{dT}{dt} = \frac{g}{C_p} * \frac{\Delta F_{\text{Atmos}}}{\Delta P}
\]

where \(\frac{dT}{dt}\) represent heating rate measured in °K/day, \(g\) is the acceleration due to gravity (9.8 m s\(^{-2}\)), \(\Delta F_{\text{Atmos}}\) denote the atmospheric forcing, \(C_p\) represents specific heat of air at constant pressure whose value is 1006 J kg\(^{-1}\) K\(^{-1}\) and \(\Delta P\) is the difference in atmospheric pressure between TOA and SRF boundaries where most of the aerosols exist and its value is considered as 300 hPa.

\[\text{(1.7)}\]

Figure 1.3: Estimated annual and global average energy balance [47]

1.9 Motivation of the Study and Statement of the Problem

The earth’s environment is constantly evolving owing to increasing human population and their corresponding activities leading to pollutant emissions. Industrial activities, land use and combustion of fossil fuels emit greenhouse gases and aerosols, resulting in the change of atmospheric composition [48, 49]. Aerosols can impact air quality, public health and climate.

Glacier melting due to light-absorbing aerosol has become a growing concern in the recent decades. Due to its absorptive nature, fine size and chemical characteristics, interest in
BC has increased. At Himalaya the deposition of BC aerosols on snow surfaces has accelerated snow melt and glacier retreat [50]. A huge quantity of BC aerosols can be migrated from long range i.e. Indo-Gangetic plain and beyond into the Himalayan region, apart from the local emission as reported by previous researchers [51-54]. Over various locations of Himalayan, mountain breeze circulations also bring a significant amount of BC aerosol [55]. These migrated BC aerosols would increase the warming over the Himalayan regions considerably earlier than the coming of summer and monsoon seasons [14]. Mineral dust changes the albedo of glacier surfaces, which in turn change the melting rate of glaciers and seasonal snow [56]. There are different sources of dust deposited on glaciers [57].

The prominent mountain series like Himalaya, Karakorum and Hindukush join in the extreme north of Pakistan, which are occupied by glaciers. There are >5000 glaciers in the Pakistani geographical area feeding the Indus River. The frozen water resources are decreasing continuously due to global warming effects, which reduce ice mass. The increasing trend in temperature has been observed during the last decade in the northern part of Pakistan, which enhances the snow/ice melt [58], affecting agriculture, drinking water supplies and hydroelectric power, amongst other societally-relevant necessities. The melting rate also increases the threat of glacier related hazards, including Glacial Lake Outburst Floods, which are among the remarkable risks [59].

The interaction of radiations with aerosols depends on the size, shape and composition of particles, which in turn leads to varying effects on the climate, cloud formation, precipitation and public health. PM$_{10}$, PM$_{2.5}$ and ultra-fine aerosols have different characteristics, sources and potential health effects. There is a clear association between the concentration of PM and health effects [1, 60, 61]. Particularly the fine PM fraction can more easily penetrate into the lungs and cause respiratory diseases [62, 63]. BC aerosol in particular can damage the cells of the human body and lead to cancer. To know the effects of PM on human health and climate
is of great importance. The morphological and chemical characterization of PM has attained significant importance in the recent years, because such data are needed to accurately constrain aerosol radiative properties [64] and health impacts [65].

The forcing implications over the glacier region are very crucial for climate modelling tasks and adaptation to the potential effects of the change in melting rates of ice. As BC aerosols have an important role on the melting of Himalayan glaciers and on radiative forcing, therefore its study over high-altitude sites at Himalaya has a special importance [53]. The information about BC over these high altitude locations is very helpful for the understanding of local and regional weather and climate change. The aims and objectives of the present research work are to study the morphology, size and chemical composition of the aerosols. The frequency of different particle types based on their classification into categories according to their elemental composition and morphology are also quantified. Moreover, the optical properties, characterization, variability and climatic effects of aerosols are also carried out over the study locations.
Chapter 2

Literature Review

In order to understand the current climate change, the analysis of aerosol properties and their radiative effects are very important. Therefore, a step-by-step review of the published literature is given below.

2.1 Analysis of PM Concentration, Morphology and Composition

Satsangi et al. [66] determined the chemical composition and morphology of PM$_{2.5}$ by using valuable technique i.e. Scanning Electron Microscopy (SEM) attached with Energy Dispersive X-ray Spectrometry (EDX) and mineralogy with X-Ray Diffraction (XRD) over Indian city (Pune) from 2010 to 2011 between June and September. From these analytical techniques, they found different chemical compositions i.e. silicates, oxides, sulfates, phosphates and carbonates. They found that Si were dominant among all the elements. The main sources of PM were building and soil materials, oil combustion and biomass burning.

Pachauri et al. [67] collected PM on Quartz filter with High Volume Sampler at Agra (India) from January to June 2010 and then find the chemical composition, morphology and size through SEM-EDS. They reported particles of larger size with diameter ranged from 2 to 70 µm. They divide the analyzed particles into three groups namely Geogenic, anthropogenic and biogenic particles. The particles in each group have different morphologies. They documented the total PM mass concentration of 306.1 µg/m$^3$. The highest concentration was noted in winter (338.6 ± 89.1 µg/m$^3$) followed by summer (273.4 ± 85.5 µg/m$^3$).

Alam et al. [1] studied aerosol mass concentration and their size distribution over four cities in Pakistan (Karachi, Lahore, Rawalpindi and Peshawar) by using GRIMM instrument during March and April 2010. They found that the 24 h average PM$_{2.5}$ mass concentration were 185, 91, 140 and 160 µg/m$^3$, for Karachi, Lahore, Rawalpindi and Peshawar, respectively. Likewise, the 24 h average PM$_{10}$ concentrations over the above locations were 461, 198, 448
and 540 µg/m³, respectively. The noted sources of these high concentrations of PM in each city were due to the industrial emission, vehicular emission, re-suspension of dust and sea salt particles.

Alam et al. [68] characterized the collected samples of PM₁₀ for various chemical compositions in the city of Lahore. They documented that the concentration of PM₁₀, OC and EC were 486 ± 87 µg/m³, 63 ± 42 µg/m³ and 21 ± 15 µg/m³, respectively. They point out the four main sources of PM₁₀ in Lahore like industrial emission, vehicular emission, re-suspended dust and biomass burning.

Alam et al. [2] determined PM concentration, sources, size and volume distribution by using GRIMM instrument in Peshawar city during April 2011. They reported the PM₂.₅ mass concentrations of 172 µg/m³ and that of PM₁₀ of 480 µg/m³ in the city. With the help of a model called Positive Matrix Factorization (PMF), they also identified five sources of PM namely vehicular, industrial, brick kiln, household combustion emissions, re-suspended road and soil dust.

Anake et al. [69] reported the morphology, composition and sources of PM by using SEM attached with EDX in Agbara (Nigeria) during October–December, 2014. The authors observed Si and C in highest amount as compared to other elements. The identified sources were industrial emission, vehicular emission, dust and solid waste combustion. Hamdan et al. [70] collected samples (indoor and outdoor) of both PM₂.₅ and PM₁₀ on Teflon filter papers by using Low Volume Sampler (LVS) in United Arab Emirates (UAE) and then analyzed for the chemical composition. They attributed the coarse particles to the natural origin (crustal, sea salt and dust) but fine and ultra-fine particles to both natural and anthropogenic (SO₂ and NOₓ) sources.

Engelbrecht et al. [71] studied the chemical and physical properties of dust collected from the Middle East countries namely Djibouti, Iraq, Kuwait, Afghanistan, UAE and Qatar for a
period of 1 year. They used different techniques like XRD (mineralogy), SEM-EDS (chemical composition), XRF (trace elements) and ICP-MS (major elements). They investigate three main types of PM i.e. geological, smoke and heavy metals. Edgerton et al. [72] measured OC and EC after sample collection of both PM$_{2.5}$ and PM$_{10}$ on Quartz fiber filter in urban and rural location of United States. They used techniques such as SEM-EDS for the determination of individual carbonaceous particles. Computer Controlled Scanning Electron Microscopy (CCSEM) results indicate that on average, biological particle like pollen, vegetative debris and fungal spores whose concentration varied from 2 to 16 µg/m$^3$ and account for 60 to 70 % of the carbonaceous particles in both PM$_{2.5}$ and PM$_{10}$ samples. SEM result revealed that at urban location the PM (PM$_{2.5}$ and PM$_{10}$) concentration varied from 25 – 42 µg/m$^3$, which was produced due to industrial emission.

Fu et al. [73] find out morphology and chemical composition of individual carbonaceous particle in Shanghai (China) during November-December (2010) by using Transmission Electron Microscopy attached with (EDX). They divide the analyzed carbonaceous particles into four groups i.e. polymeric organic compound, soot, tar ball and biogenic particle. Their results shows that the most dominant particles found were sulphates (38–71%) and soot (11–22%). But, soil related particles (68%) were found more frequently during a dust storm day.

Kgabi [74] collected PM on filter paper by using Tapered Element Oscillating Microbalance (TEOM). After sampling, they determined the elemental composition and toxic metals with the help of various techniques. The following elements were investigated by using SEM-EDS namely Mg, K, Na, C, O, F, S, Si and Fe. Similarly the ICP-MS analysis find out the elements like Ca, Al, Mg, K, Na, Cu, Zn, Mn, Ni, Cr, Pb and Fe.

Ault et al. [75] conducted a single-particle analysis and spatio-temporal variations of Iron-containing coarse PM, which were collected passively in Cleveland, Ohio (Urban environment) during August to September (2008), July to August (2009) and February to
March (2010). For this purpose, they used a combine technique of X-ray elemental mapping and CCSEM-EDX. The results revealed that the fly ash concentration was maximum in Flats sites and minimum outside this location. They attributed the variation in fly ash concentration to the annually changes in steel production. From the morphology point of view, fly ash particles were spherical in Flat location, while found less spherical away from this location which is due to atmospheric processes like combustion, coagulation and atmospheric reactions. Katchko et al. [76] collected fly ash particles from nine power plants and characterized them through SEM-EDS. They found that all fly ash particles have spherical morphology and contains mainly of alumino-silicate spheres (amorphous) along with Iron rich spherical particles in minor amount. The elements present in fly ash were Si, Al, Fe, Ca and O. The minor elements like K, Mg, Na, Ti and S were observed with Si and Al. They also noted that Ba was the only trace element presents.

Slezakova et al. [77] characterize PM$_{2.5}$ and PM$_{10}$ emitted during traffic in the city of Oporo (Portugal) during 2005. They analyzed 1,000 individual particles through SEM-EDS and found their morphology and chemical composition. They also analyze the particles taken from background sites and find various types of particles present in the collected PM by using cluster analysis. Aluminum silicate particles were the majority particles found in the background PM$_{2.5}$, which mainly produce from natural sources. Aluminum silicate particles were found to be 74% and 73% for traffic and background locations in PM$_{2.5-10}$, respectively. They concluded that PM$_{2.5}$ mainly consists of traffic related particles but coarse particles were mainly produce from natural sources.

### 2.2 Analysis of the Aerosol Optical Properties and Assessment of Radiative Forcing

Eck et al. [78] conducted multiyears research study of the aerosol properties and their climatological aspects over three locations (Bijing, Kanpur and Ilorin). They carried out study
about the opticle properties like AOD, SSA and other parameters. Mariq et al. [79] measured the optical characteristics and radiative forcing of aerosols over high altitude (5100 m amsl) over Himalayan range at Nepal Climate Observatory – pyramid region for a period of 3-years. They noted the value of monthly average scattering coefficients varied between 0.1 Mm\(^{-1}\) and 20 Mm\(^{-1}\), but the mean absorption coefficient varied between 0.5 Mm\(^{-1}\) and 3.5 Mm\(^{-1}\), respectively. Maximum values of both parameters were reported in April, while minimum in July and August. They also reported the aerosols direct radiative forcing at TOA at a distance of 500 m from the surface to be range from 10-20 W/m\(^2\) and radiative forcing at SRF varied from -4 to -20 W/m\(^2\).

Over Delhi, Tiwari et al. [80] measured the variation in aerosol optical properties and their frequency distribution for a period of 2-years. They reported high value of AOD (June and November) and low value (March and September) over the study site. Seasonally maximum AOD and AE values of 1.0 ± 0.42 and 1.02 ± 0.16 were reported during post-monsoon season while their minimum values of 0.95 ± 0.36 and 1.02 ± 0.20 were noted during winter season. They also computed five days backward trajectories of air masses. Ram et al. (2016) [81] studied the variations in the aerosol properties during haze and dust episodes at Kanpur (India) from January (2007) to March (2008). They reported that the value of absorption coefficient range from 8.3 to 95.2 Mm\(^{-1}\) and that of scattering coefficient ranged from 58 to 564 Mm\(^{-1}\). They also documented that SSA ranged from 0.65 – 0.92 and AAE varied from 0.79 -1.40 during pre-monsoon and winter season.

Xu et al. [82] measured the variability of aerosols over Tibetan Pleatu (TP). Moreover, they also studied aerosols sub-types by utilizing 8-years of CALIPSO data. They reported maximum value of AOD during spring and summer. Over northern part of TP, maximum AOD values were found in the month of May, while over southern part maximum AOD values were reported in July. Higher monthly AOD were found over northern as compared to
southern part. They also documented dust as major aerosols types, which more affect the environments of TP as compared to the polluted dust and smoke. Ali et al. [83] conducted study on the seasonal variation of AOD retrieved from MODIS satellite over various locations of Saudi Arabia for a long period from 2002-2013. They also performed the trend analysis and frequency distribution of AOD during different seasons.

Kaskaoutis et al. [84] studied the aerosol properties and its trends analysis at Kanpur (India) from 2001 to 2010 by using AERONET data. They observed the increasing trend of AOD during October to February and neutral or decreasing trend during March to September. They attributed the increasing trend of AOD to the anthropogenic activities, while decreasing trend to dust outbreak. Dumka et al. [85] investigated the variations in the aerosol properties latitudinal wise e.g. from Indo Gangetic plane (IGP) to Himalaya foothills during pre-monsoon season of two years i.e. 2008 and 2009. They measured AOD over four locations of different environment namely Naintal, Pantnagar, Bareilly and Kanpur. They observed that AOD increases from Naintal (Himalaya) to Kanpur (IGP). They reported the radiative forcing at TOA (-7.61 and -17.63 W/m$^2$), SRF (-45.75 and -73.07 W/m$^2$) and within ATM (38.14 and 55.43 W/m$^2$) over Naintal and Kanpur, respectively. They also calculated Heating Rate (1.07, 1.41, 1.58 and 1.56 K/day) for the above four locations, respectively.

Gautam et al. [86] investigated the aerosol properties, radiative effects and their distribution over IGP and along the southern slope of Himalayan region during spring (2009). They found high AOD (0.6) in April–June, which are due to the passage of dust from arid location of south west Asia to IGP. They noted the value of SSA<0.9 at a wavelength of 550 nm suggesting absorbing dust over IGP. On the other hand, less dust transport is observed in the southern part of IGP and Himalayan slope. They documented lower SSA in the range of 0.85 to 0.9 at wavelengths of 440-1020 nm over Himalayan slope at Nepal region indicating more
absorbing aerosols (strongly absorbing haze) than IGP. Moreover, during spring they also observed the lifting of aerosols along the slopes of Himalaya.

Ram et al. [87] carried out long time study of PM from February (2005) to July (2010) about chemical composition and its optical properties over Monora peak (Himalaya). They documented that PM concentration ranged between 13 and 272 µg/m³ throughout the study period. They also reported that both PM and AOD increases from April to June associated with the transportation of dust from desert regions to the receptor site. They also noted high value of OC and EC during September to March and low value from July to August. Ramana et al. [88] studied the ARF during winter season of 2003 over three different locations in Nepal situated in the Himalayan region. They reported that AOD varies from 0.20 - 0.34 and SSA from 0.7 - 0.9 attributed to the absorbing aerosols. They noted average diurnal aerosol surface radiative forcing efficiency of -73 W/m², average seasonal reduction in solar flux of 25 W/m² and heating rate of 1 °K/day over the region.

Sing et al. [89] reported the properties and surface radiative forcing of aerosol at Delhi during (2003) from (April–June). They measured AOD at visible and near infrared radiation region and the total average ARF efficiency at the surface (280 to 2800 nm) and then matched with the value obtained through SBDART model. They used OPAC model and showed that a mixture of aerosol consist of desert dust and urban aerosols. The AE value indicated the load of dust aerosol during the study period. They reported a very low value of SSA (0.67).

Toledano et al. [90] conducted research on the characterization and classification of aerosol through basic optical parameter i.e. AOD and AE for two years from 2002 to 2004 over EI Arenosillo (Spain). They attributed high value of AOD and low value of AE to the dust. They documented the average value of AOD and AE were 0.18 ± 0.14 and 1.05 ± 0.43, respectively. They reported the maximum AOD during summer and at the end of winter, which they attributed to the seasonal dust. They also noted two frequency mode of AE, which
were related to two types of aerosol namely coastal marine and dust aerosols. Wang et al. [91] conducted long-term study on the AOD, AE and SSA at urban environment of Wuhan (China) from (2007 to 2013). The maximum value of AOD (1.52) was reported in June 2012 and minimum (0.57) in November (2012) and the maximum value of AE (1.71) was documented in June (2010) while minimum (0.78) during April (2012). From the study of AOD and AE they concluded that in the region the fine mode aerosol particles were dominant.

Yu et al. [92] studied the seasonal alterations in aerosol characteristics and their radiative effects at Beijing for long time period from March (2001) to March (2015). The maximum AOD value was reported during (spring and summer) while minimum during (fall and winter). Among the four seasons the lower value of AE were found in spring season, which indicate the occurrence of dust particles in aerosols size distribution. They also documented the average ARF at the TOA were -33 ± 22 W/m² (spring), -35 ± 22 W/m² (summer), -28 ± 20 W/m² (fall) and -24 ± 23 W/m² (winter). Guleria et al. [93] investigated the aerosol properties for 1-year period from April to March (2006) over Mohal. They reported high value of AOD and low value of AE during summer season, which correspond to comparative large quantity of coarse particles.

2.3 Monitoring and Measurement of BC Aerosols

BC aerosol is a type of atmospheric carbonaceous aerosol particles, which has strong ability to absorb solar radiations. The emergent literature is available about the change of the regional and global climate due to the existence of BC aerosols. In the present section, a step-by-step literature review conducted by different researchers at different locations is described. Babu et al. [54] studied the BC variation, seasonality and sources apportionment over Hanle (4520 m amsl) over round the year i.e. August 2009 to July 2010 using Aethalometer. They reported that the daily average concentrations of BC aerosols varied from 7 ng/m³ – 296
ng/m³ with the annual mean of 77 ± 64 ng/m³. According to them, the BC concentration was highest during March–May and lowest during December–February. Seasonally, the highest BC concentration of 109 ± 78 ng/m³ was noted during spring (June-August) followed by 66 ± 42 ng/m³ during winter (December-February).

Raju et al. [94] studied the mass concentrations of BC over Sinhagad (India), a high altitude rural location with Aethalometer during the two seasons (pre-monsoon and post-monsoon) from 2009 – 2010. They found maximum average mass concentration of BC aerosol during post-monsoon than during pre-monsoon in the study period. Similarly they also reported that BC has a good correlation with RH and Temp (in Pre monsoon), but in Post-monsoon a low correlation was found with Temp and good correlation with RH only during night hours.

Dumka et al. [95] carried out 7-channel Aethalometer based studies of the mass concentration of BC at Monora Peak (central Himalaya) (November 2004–December 2007). They documented higher mean BC mass concentration during spring (1.34 ± 0.05µg/m³) followed by autumn (1.03 ± 0.0405µg/m³) and summer (0.53 ± 0.0205µg/m³ with overall average of 0.99 ± 0.02 µg/m³. They also observed well-define daily variation with single peak in the late afternoon time from the month of October to March, while noted insignificant variations from April to September. They also reported that daytime mass concentration of BC was higher by a factor of 2 as compare to night time BC mass concentration.

Safai et al. [96] conducted 1 year Aethalometer based study of BC concentration at Pune (urban Indian location) from January to December. They documented high BC mass concentration during winter and low during monsoon with overall average concentration of 4.1 µg/m³ for the study period. They also observed morning and evening peaks and attributed to diurnal changes in the local boundary layers. They reported that over the study site the BC aerosol have contributions of 2.3% in the total aerosol mass.
Latha and Badarinath [97] carried out studies on the determination of total BC mass concentration and their seasonal variation as well as their relationship with meteorological parameter over Hyderabad, a 5th largest city in India, January to December (2003) using Aethalometer. They reported maximum BC concentration of 10 µg/m³ (November – April) and low concentration of 4 µg/m³ (June – October) over the city. They also studied the daily variation of BC concentration and observed morning peak from 7: 00 to 9: 00 LST and a wide peak during nighttime from 21: 00 to 02: 00 LST, with high nighttime and low daytime BC concentration. They also observed a positive association of BC with Temp and WS and noted negative link with RH and RF.

Pant et al. [98] measured the mass concentration of BC by using Aethalometer over Monora peak, high altitude station lies in central Himalayans region during December 2004. They reported an average BC mass concentration of 1.36 ± 0.99 µg/m³ and attributed it to the human activities as well as to the boundary layer dynamics. They also calculated aerosol radiative forcing at SRF (-4.2 W/m²), TOA (+0.7 W/m²) and within ATM (+4.9 W/m²). The forcing per unit optical depth (forcing efficiency) was calculated to be nearly 88 W/m², which corresponds to great fraction of BC mass concentration.

Begum et al. [99] conducted Aethalometer based BC study over eight locations in India selected from mainland, Island and highland from January to May (2006). They noted maximum value of 27 µg/m³ over an urban sites while minimum value of 0.065µg/m³ over Arabian Sea. They also observed diurnal variation and point out that BC having high values during night and low during afternoon time over mainland and Iceland, while for high land sites they noted afternoon high and early morning low concentration. Tripathi et al. [100] carried the Aethalometer based study of BC concentration over urban location Kanpur during December 2004. They observed BC concentration ranged from 6 to 20 µg/m³. They also
measured aerosol radiative forcing at SRF (-62 ± 23W/m²), TOA (+9 ± 23W/m²) and within ATM (+71W/m²) over the location.

Tiwari et al. [26] studied the variation of BC at urban environment of New Delhi (India) for one-year period during 2011 by using Aethalometer. Moreover, they also measured the relationship of BC concentration with meteorological parameter like Temperature, mixed layer depth, RH, WS, and VIS. They found the contribution of BC aerosols is about 6% of the total PM$_{2.5}$ mass. Bibi et al. [101] studied the temporal variation (diurnally, monthly and seasonally) of BC concentration over an urban environment Karachi, Pakistan for 2-year study from 2006 to 2008 using Aethalometer observations at each 5-min interval. They also observed the relationships of BC aerosol concentration with meteorological parameters (Temp, RH, WS, Vis and RF). They reported that BC has inverse relationship with all meteorological parameters.

Kalluri et al. [102] studied the variation of BC as well as ARF at Anantapur (India) from January 2013 to December 2014. They noted highest and lowest value of BC mass concentration of 3.4 ± 1.2 µg/m$^3$ and 1.1 ± 0.2 µg/m$^3$ during January and July, respectively. They calculated radiative forcing within ATM were +36.8 ± 1.7W/m² (summer), +26.9 ± 0.2 W/m² (winter), +18.0 ± 0.6 W/m² (monsoon) and +18.5 ± 3.1 W/m² (post monsoon). The morning peak observed between 07:00-08:00 LST and evening at 19:00 to 21:00 LST and one minimum peak also observed between 13:00 and 16:00 LST. Bibi et al. [103] carried out study of BC aerosols mass concentration and their optical and radiative properties over Karachi from March (2006)–December (2008). The maximum value of BC concentration was reported in January 2007 and minimum in June 2006. Similarly, the authors reported positive net ARF at the TOA and within atmosphere, while negative at Surface.

Zhang et al. [104] measured the mass concentration of BC from June 2012 to May 2013 over Hefei city of China by using Aethalometer. They studied the temporal variation of BC mass
concentration in different time scale (diurnal, monthly and seasonal) along with the identification of different sources of BC concentration. Begam et al. [105] carried out 7 channel Aethalometer based study for the characterization of the mass concentration of BC from September 2011–November 2012 over Kadapa city of India. They studied the BC concentration diurnally, monthly and seasonally during the study period. They also find out BC correlation with various meteorological parameters like Temp, WS and RF. Bisht et al. [106] conducted Aethalometer based research on the variation of BC concentration over an urban environment of Delhi (India) during 2012. They also investigated the effect of BC concentration on various optical parameters. Moreover, they also studied the radiative impacts of BC and its atmospheric heating rate.
Chapter 3

Description of the Study Area, Instrumentation and Methodology

In this chapter, we discussed about the study areas, various ground and satellite instruments and the methods used.

3.1 Study Areas

The study area consists of three (03) locations in the northern Pakistan e.g. Peshawar, High altitude glacier areas and Dir (Upper) as shown in Figure 3.1.

3.1.1 Peshawar

Peshawar (34.03 °N, 71.56 °E) is the historical as well as the capital city of the Khyber Pahktunkhwa as shown in Figure 3.1. Its altitude is 359 m (amsl) and covers an area of 1,257 km². The population of the city is about 4 million and increasing continuously, because of the migration of peoples in search of jobs and education etc. [2]. The rapid urbanization is creating greater vehicular traffic in the city. There are various industries in this city including textiles, paper, furniture, pharmaceuticals, steel, cigarettes, cardboard and food processing. There are also many steel industries in Peshawar city [2]. Peshawar is hot during summer (May-August) having an average maximum temperature of 40°C. It has cold winters (November-March) with a maximum mean temperature of 10°C. Sampling was performed in the Pakistan Metrological Department (PMD) building, which is close to a roadside. PMD is situated in the core of the old city and is surrounded by various residential areas, roads, fly over and is exposed to emissions from high vehicular traffic.

3.1.2 High Altitude Glaciated Area

The three world well-known mountain ranges (i.e., Himalayas, Karakoram and Hindu Kush (HKH)) are joined together in the extreme north of Pakistan. These high altitude stations are very glacial. The glacier areas in Pakistan are spread over an area of about 16933 km² and
consist of high altitude peaks and lakes. The details of the locations, where we have carried out research are given below.

Astore (35°21′24″N, 74°48′22″E, 2600 m amsl) is the district of Diamer division of Gilgit-Baltistan having total area of 5092 km² and its capital name is Eidghah. According to the 1998 Pakistan census, the population of this district was 71,666. The environment of Astore is pleasurable, dirt-free and fresh. Thick jungles, towering elevations and wide grasslands enhance the natural beauty of the location. Astore lies on the base of the words 9th highest peak Nanga-Parbat (8126 m).

Gilgit (35°52′43″N, 74°25′2″E, 1500 m amsl), is one of the district of Gilgit divisions of Gilgit-Baltistan and Gilgit is its capital city which is situated near the Gilgit and Hunza river. Gilgit is a centre for mountaineering expeditions. Its total area and population are 38000 km² and 243,324, respectively. Distaghil Sar is the highest peak in the district which is 7885 m high, being a 19th highest peak in the word and 7th in Pakistan.

Sost (36°41′28″N, 74°49′7″E, 2790 m amsl), a part of Gilgit division, lies in the upper Hunza and is the last town coming on Karakorum High way inside the Pakistan, beyond which China Boarder starts. All the traffic from China-Pakistan boarder are passing from this town that is why Sost is an important place for passenger and cargo. Sost port connects Pakistani cities of Gilgit and Chilas on the south to the Chinese cities of Tashkurgan and Kashgar in the north.

Skardu (35°14′34″N, 75°37′55″E, 2680 m amsl), district is a region of Baltistan and its capital name is also Skardu. Its total area and populations are 15,000 km² and 214,448, respectively. Several lofty mountains included in Skardu, which attract climbers from all over the word. Biafo, Baltoro glacier and the world second highest peak i.e. K2 (8611 m), Gasherbrum’s, Trango tower and Broad peak lies in Skardu district. Skardu town situated on
the Indus River, which provides a gateway to the Karakoram ranges and separate Karakorum from Himalaya.

3.1.3 Dir Upper
Dir (upper) lies is in the northwestern Pakistan (35.20°N, 71.87°E) and spread over an area of 3,699 km². The geography of Upper Dir is dominated by high mountains. The Hindu Kush is the well-known mountain range in Dir Upper. In winter, the whole area remains snow-covered. Dir (upper) mountain peaks rising to 4,900 m amsl in the northeast. The main river of this area is Panjkora River, which originates from Kohistan having a length 220 km. The river's headwaters are high on the glaciers of Hindu Kush Mountains. Its weather is pleasant during summer, but during winter temperature drops below the freezing point. Table 3.1 summarize longitude, latitude and study period of the study locations.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location Coordinates</th>
<th>Altitudes</th>
<th>Measurement period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astore</td>
<td>35°21'24&quot;N, 74°48'22&quot;E,</td>
<td>2600 m amsl</td>
<td>i 2004 to 2016 ii Nov, May 2016</td>
</tr>
<tr>
<td>Gilgit</td>
<td>35°52'43&quot;N, 74°25'2&quot;E,</td>
<td>1500 m amsl</td>
<td>i 2004 to 2016 ii May, Nov and Dec 2016</td>
</tr>
<tr>
<td>Sost</td>
<td>36°41'28&quot;N, 74°49'7&quot;E,</td>
<td>2790 m amsl</td>
<td>May, Jun, and December 2016</td>
</tr>
<tr>
<td>Skardu</td>
<td>35°14'34&quot;N, 75°37'55&quot;E,</td>
<td>2680 m amsl</td>
<td>i 2004 to 2016 ii Dec and Jun 2016</td>
</tr>
<tr>
<td>Peshawar</td>
<td>34.03° N, 71.56° E</td>
<td>395 m amsl</td>
<td>November 2016</td>
</tr>
<tr>
<td>Dir (Upper)</td>
<td>35.20° N, 71.87° E</td>
<td>1420 m amsl</td>
<td>2004 to 2016</td>
</tr>
</tbody>
</table>
3.2 Instrumentation

3.2.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a high resolution and great magnification imaging technique. SEM provides the details about Topography (surface feature and texture), composition (elements present) and Morphology (Size, Shape and particles arrangement) of ambient PM$_{2.5}$ and PM$_{10}$. SEM uses a beam of electron, which is focussed on the sample, scan the surface and generate a variety of signals. In SEM analysis, there are three most common modes of operation i.e. Backscattered Electron Imaging (BSE), Secondary Electron Imaging (SEI) and Energy Dispersive X-ray Spectroscopy (EDX). Back scattered electrons are the electrons of high-energy, which are reflected directly from the surface of the sample. BSE gives details of the atomic number and about topography. SEI gives topographic...
information. EDX gives the details of the chemical structure of the sample. EDX collects the X-rays ejected from the sample, when the sample is strike by the beam of electrons.

In the present study, SEM-EDX was utilized for the PM characterization. The PM produced from different sources was identified with the help of morphology and chemical composition. For SEM sample preparation, sections of 1 mm by 1 mm were cut with scissors from each particular filter paper. Thin coating of gold was made on the sample, with the help of a Gold Sputter Coater. This will make the surface of the sample conductive and reduce electronic charge as well. The sputter can prepare six samples simultaneously. In the SEM-EDX compartment, the samples were kept in the corner and double images were taken for each sample. To analyse coarse particles, a microscope magnification of 550 was used with field of detection (60×150 μm). Ten random particles were selected on each field and about 20 fields per every particular filter were detected, giving nearly 200 manually characterized particles on each filter. As a whole, 12,000 particles were analysed for 60 samples. For the analysis of particle morphology and location, the back-scattered electron mode was used. For every signal, there is an installed detector that detects its corresponding signal and rejects others. The background or unwanted signals were therefore blocked in this way. The applied working conditions were: X-ray limit of detection = ~0.1%; X-ray spectrum acquisition live time = 60 s; detector (20 mm) away from the samples = Si. For each examined filter substrate, the results were taken from three randomly selected fields, which provided representative results to minimize subjectivity.

3.2.2 Fourier Transform Infrared (FTIR) Spectroscopy
FTIR spectroscopy is a vital non-destructive analytical technique used to detect various kinds of functional groups and bond in molecules (organic or inorganic). FTIR spectrometer comprises of interferometer, radiation source, detector, sample and computer as shown in the Figure 3.2. The main parts of interferometer are beam splitter, fixed mirror and moving mirror. The beam splitter divides the incident radiations into two parts. The beam reflected
from both fixed and movable mirror recombines in the beam splitter, produce interference. After the measurement of the interference, a graph called “interferogram” is achieved. The interferogram is detected by the installed detectors and direct it to computer, where a mathematical calculation of Fourier transform is performed.

FT-IR spectra were acquired with Perkin Elmer Spectrum Two equipped with UATR (Universal Attenuated Total Reflectance). Before taking data for a sample, a background scan was conducted. Each spectrum is an average of 200 scans and quantifies the transmission of infrared radiation as a function of wave number. These Spectra were recorded over a wide spectral range from 4000 to 450 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). FT-IR spectrometer was used to analyse the samples directly on quartz filters without sample preparation. The spectrum of the loaded filter automatically subtracted from that of unloaded filter, yielding information about the PM on the filter. This method has been used by the previous researchers for the detection of organic functional groups such as carbonyls, aliphatic carbons, nitrates and sulfates [107]

**Figure 3.2**: Schematic diagram of FT-IR [108]
3.2.3 Moderate Resolution Imaging Spectroradiometer (MODIS)

MODIS is a device that is functionalized on Terra and Aqua satellites and was put into orbit by NASA since 1999 (December) and 2002 (May), respectively. Terra's satellite revolving around the earth across equator from north – south (morning time), while Aqua orbiting over the equator from south – north (afternoon time). There are 36 channels of MODIS instruments ranged from 0.14 – 14 µm that gives the data on atmospheric, terrestrial and oceanic backgrounds. There are diverse approaches used by MODIS instruments for the retrieval of data over land [109] and oceans [110]. MODIS also provides day time data of many aerosol parameters at a spatial resolution of 10 km. Snow/ice cover places and Sahara Desert are high albedo regions for MODIS, cause large uncertainties in the model and ground analysis [111]. Due to the high reflectance, MODIS instruments cannot easily differentiate between land surface and atmospheric aerosols [112]. Therefore for the improvement in the data (quality and accuracy); the MODIS algorithms have been restructured to modify the surface reflectance database, cloud masking process and aerosol models [113]. A very key improvement in the aerosol products (MODIS level 2) is the addition of Deep-Blue algorithm, which retrieves aerosols properties over bright land surfaces including Sahara Desert.

In the current research work, MODIS-Aqua (MYDO8) level 3.0 QA columnar water vapour data have been used. MODIS-Aqua also been used for the retrieval of haze images during haze period in November 2016 in Peshawar. MODIS AOD data were also used for Dir (Upper) during 2004 – 2016.
Figure 3. 3: MODIS satellite [114].

3.2.4 Ozone Monitoring Instrument (OMI)

OMI was established in July (2004) (see Figure 3.4). OMI instrument is replacement of the satellite (Total Ozone Mapping Spectrometers) and is design to continuously observe not only ozone but earth climate and air quality as well [115]. OMI has high spatial and spectral resolution, has wide-ranging swath and provides daily data [116]. OMI instrument observes the scattered radiations by the atmospheric aerosol at wavelength (270 – 500 nm). OMI satellite has nadir-viewing that observe upwelling radiances at TOA in the solar spectrum [116].

OMI is able to detect layers of absorbing aerosol at the wavelength of around 400 nm. Torres et al. [117] provided a detail method of obtaining the Ultraviolet (UV) AI using the “near UV Aerosol Retrievals (OMAERUV)” algorithm, which can detect absorbing aerosol (desert dust and carbonaceous aerosol). For the current research work, an improved daily Level 2 (1°x1°) OMAERUV version 3 AOD data product, daily Level 3 (1°x1°) OMT03d (version 3) AI data, daily level 2 (10 x 10 km) OMAERUV (version 3) AAOD data and Level 2 (0.25°x0.25°) OMAERUV (version 3) daily SSA data product at 500 nm were used. Furthermore, for the measurement of BC radiative forcing, columnar ozone data during the study period were also used.
3.2.5 Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO)

This satellite was established on 28 April 2006 and is shown in Figure 3.5. The equatorial crossing times of CALIPSO are about 13:30 and 01:30, with a repeating cycle of 16 days [118]. It observes the spreading of clouds and aerosols in vertical profile of the atmosphere on local as well as on global level. At this time CALIPSO is the only satellite in the orbit that delivers information of aerosols vertical profile and 3-dimensional spreading of aerosol properties. It can identify atmospheric aerosols over bright surfaces, in clear sky environments and below thin clouds [119, 120] and this is the contrasting property of CALIPSO as compared to other satellite remote sensing instruments. A Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) instrument delivers constant measurements of attenuated backscatter radiations during day/night with perpendicular and parallel polarization components around the entire globe. Observation from CALIPSO instruments offers major improvements in our understanding of judgment of different types of aerosols. In the current research work, CALIPSO Level 2.0 (version 3.30) data was used.
3.2.6 The Clouds and the Earth’s Radiant Energy System (CERES)

The CERES instrument is an important constituent of the Earth Observing System (EOS) program, which started in 1998. CERES instrument observes the infinitesimal variations occurring in the Earth's energy balance and also determines the difference between incoming and outgoing energy. The CERES instrument measures the fluxes at TOP, SRF and within ATM at several selected levels [121]. Details about the CERES dataset are available on the CERES website (http://ceres.larc.nasa.gov/).

3.2.7 Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model

HYSPLIT model can be used for the calculation of specific trajectories of air masses (forward as well as backward) [122]. In this present study, we have used this model for
specific days representing each months / seasons at different height (500, 1000 and 1500 m) above the earth surface during the full studied period.

3.2.8 Aethalometer

Over four high altitude locations, the BC were measured with Magee Scientific Model AE21 Aethalometer. The flow rate of Aethalometer was kept at 5 LPM and the wavelength channel of 880 nm was selected. The data was recorded at the interval of fifteen minutes. At 880 nm wavelength, BC has maximum absorption capability, therefore for the measurement of BC mass concentration; the 880 nm wavelength is generally applied. It measured the mass concentration of BC aerosols by determining the attenuation of radiation produced by accumulated BC on quartz filter strips with backing of cellulose. The applied radiations are of great intensity having wavelengths (880 and 370 nm), respectively [123]. For the BC measurement, Aethalometer use the method of optical transmission and filtration [124]. The vacuum pump of Aethalometer constantly sucking air and particles accumulate on the filter strip. Beams of light are allowed to passes through both loaded and unloaded filters and then inter compared with each other.

There are a number of systematic errors found in Aethalometer, which basically works on the absorption methods that needs to be rectified [125]. The measurements of BC concentration have nearly 10% uncertainty [126] owing partly to the changes in filter scattering as a function of aerosol loading [127]. In Aethalometer measurement, 20% of uncertainties are because of the scattering behaviour of light from aerosol accumulated on the filter strip [128, 129]. The detail information about the data handling, error and principles of operation of the Aethalometer has been extensively explained in previous research work [130].

In the present thesis, the Aethalometer based sampling at Astore, Gilgit, Sost and Skardu were conducted near PTDC Rama Lake, GB Scout Minawar, PTDC Motel and Sadpara Lake, respectively during May, June, November and December 2016.
3.3 Methodology

In the present work, various models were applied to determine the optical and radiative effects of aerosol.

3.3.1 Modelling

The detailed about the models are given as.

3.3.1.1 Optical Properties of Aerosols and Clouds (OPAC) Model

This model is a software bundle used for both aerosol and clouds, which was designed in 1998. It contains the detailed information about the microphysical properties of aerosols as a mixture of different constituent and clouds of various kinds [131]. There are two parts of OPAC model: The first part contains of the datasets of the microphysical and optical properties of the clouds and aerosols constituents at various wavelength and humidity. The second part is programme called FORTRON, from which the user extracts data for the calculations of the optical properties of the mixture of aerosols and clouds constituents. For ice clouds the OPAC model offered data at 67 wavelengths ranged from 0.28 to 40 µm. Likewise, for aerosols the data are accessible at 61 wavelengths ranged from 0.25 to 40 µm and at eight classes of RH e.g. 0, 50, 70, 80, 90, 95, 98 and 99 % and water clouds. Aerosols are mixture of various constituents e.g. soot, sea salt, sulfate, mineral, water soluble and insoluble aerosols. The mass concentration for 1 particle c/m$^3$ calculated with a cut-off radius (7.5 µm) for each aerosol component [131]. The dataset provide the optical and microphysical properties of ten aerosol components, six types of water clouds and three ice clouds. This model gives the optical properties (absorption and scattering coefficients, AOD, SSA, AP and phase function), which are estimated by considering the spherical shape. Hess et al. [131] described the detailed information of the model.

To run the program the following steps should be followed:
Select the mixture of aerosol type or cloud. The user may also design a new mixture of the aerosol constituent.

Adjust the height profile

Make the selection of the wavelength at which the optical properties are to be determined.

The next step is to fix the value of RH at which the calculation is to be accomplished.

In the final step, choose the desire optical parameters. These parameters are the output of the model.

3.3.1.2 Santa Barbara DISORT Atmospheric Radiative Transfer (SBDART) Model

Ricchiazzi et al. [132] established the SBDART model at the University of California. It is a software that calculates radiative transfer equation (plane parallel) in cloudy as well as in clear environments at SRF and within ATM. SBDART code performs a broad range of radiative transfer calculations. This model can calculate the thermally emitted and scattered radiations from various directions and heights. SBDART model can conduct a wide range of calculations (up to 65 atmospheric levels and 40 radiation streams). This model is very suitable for the solution of wide series of problems e.g. in the atmospheric radiative energy balance and in remote sensing as well. This algorithm involve manifold scattering in vertically plane parallel media, which is non-isothermal and in-homogenous. The radiative transfer module called DISORT, was basically developed by Stamnes et al. [133] and is used in SBDART model for integrating the radiative transfer equation.

In SBDART model there are some necessary input parameters such as AOD, SSA, Asymmetry Parameter (AP), surface reflectance, ozone and water vapour. Moreover, solar geometry and atmospheric profiles are also vital input parameters. Five types of surfaces are categorized in SBDART model namely snow, sand, lake water, ocean water and vegetation. This model has assumed six typical atmospheric profiles.
3.3.1.3 Assessment of Radiative Forcing for BC Aerosols

Accurate measurement of radiative forcing is essential for the improved climatic effects of aerosols on local and global scale. To achieve the optical properties of BC aerosols, we put the BC concentration into the model as input parameter. In OPAC model the Aethalometer derived BC mass concentration is changed into number density [131]. The OPAC model provides the optical parameters like AOD, SSA and AP for aerosol mixture. The model contains the information of aerosols verticals height, aerosol types, wavelength and Relative Humidity (RH) which have to be defined by the user. In the current research work, for the assessment of the properties (optical), the continental average model of OPAC was selected, which is suitable for the high altitude locations. The continental average model consist of the following components e.g. water soluble of 7000 per cm$^3$, insoluble of 0.4 per cm$^3$ and BC number density of 8300 per cm$^3$. In the present model, the number density of BC results in its mass concentration of 0.5 µg/m$^3$. However, the number concentration of these components was used to achieve the finest fit between model and measured value of AODs.

The number density of BC aerosol, which was obtained from the BC mass concentration, was then put in OPAC model, which results into the optical parameters (AOD, SSA and AP) at 500 nm wavelength and 50% relative humidity. The OPAC derived AOD and MODIS derived AOD were compared with each other for the corresponding aerosol constituents and its concentrations. The OPAC output optical parameters were then put in SBDART model, which gives BC ARF. Figure 3.7 represents the details of the calculation of BC radiative forcing using OPAC and SBDART models.
Figure 3.7: Diagram representing radiative forcing by using models (OPAC and SBDART)

For the estimation of ARF due to BC fraction, the optical parameters (AOD, SSA and AP) obtained from OPAC model, columnar Ozone and columnar water vapour were utilized in SBDART model. SBDART model is used for the calculation of radiative fluxes in presence and absence of aerosols. In the current research work, we have applied this model for the calculations of radiative forcing (TOP, SRF and within ATM) in SW range (0.2 – 4.0 μm) over the study sites. In SBDART model, the months from March – September were recognized as mid-latitude summer, while all other months were assumed as mid-latitude winter.
Chapter 4

On the Morphology and Composition of Particulate Matter (PM) in an Urban Environment

This chapter concern on the classification of PM in a city environment of Peshawar (Pakistan). PM samples were collected during a dense haze event in November 2016. The purposes of the study are to report on the PM mass concentration, morphology, composition and classification of various particles. The present study will help to understand the air standard and the climatic implications of the ambient aerosol in the city.

4.1 Formation of Haze and Meteorological Conditions

The meteorological conditions of Peshawar city are summarized in Figure 4.1 (a-b). There was no Rain Fall (RF) in Peshawar during November 2016 (i.e., 0 mm) and that is the only month throughout the year in which there was no RF. The recorded minimum temperature ranged from 8 °C – 14 °C (average 10 °C), while the maximum temperature varied from 18 °C – 31 °C (average 26 °C). The value of RH varied between 49 and 85 % (average 66 %). The wind speed (WS) was almost calm during the study period with some minor WS of 0.3 knots. The wind direction (WD) over the study site was predominantly North Westerly (NW).
Figure 4.1: (a-b): Prevailing meteorological conditions of Peshawar city during November 2016.
Every year, haze episodes occur between October and November in northern Pakistan, particularly at the southern slopes of Himalaya, which spread over ~100 km in the region. The haze period investigated in this study (November 2016) was taken by the NASA Aqua Moderate Resolution Imaging Spectroradiometer (MODIS) satellite, as shown in the Figure 4.2. During autumn and winter seasons, biomass burning is very common, which when combined with industrial and vehicular emissions produces spatially extensive haze in the region.

![MODIS-AQUA satellite images during the study period (November 2016) on various days.](image)

**Figure 4.2:** MODIS-AQUA satellite images during the study period (November 2016) on various days.

### 4.2 Particulate Matter Mass Concentration

Particulate Matter (PM$_{2.5}$ and PM$_{10}$) were sampled with the Low Volume Sampler (LVS) from 1 November to 30 November (2016). The daily variations in PM are shown in the Figure 4.3. The value of PM$_{2.5}$ varied from 72 to 500 µg/m$^3$ (average 286 µg/m$^3$) and PM$_{10}$ varied from 300 to 1440 µg/m$^3$ (average 638 µg/m$^3$). The WHO limits for PM$_{2.5}$ are 25 µg/m$^3$ and that for PM$_{10}$ are 50 µg/m$^3$ [2]. In the current research work, it was found that PM$_{2.5}$ and
PM$_{10}$ were 11 and 13 times greater than the WHO daily permissible limit, indicating poor air quality for Peshawar city. Zero RF during the study period contributes to the high PM concentrations. Wind from the NW direction, which is exposed to industrial sites, also contributes to high PM values. Reasons for high PM mass concentration includes re-suspension of road dust, vehicular emissions, industrial emissions, brick kiln emissions and residential combustion [1, 2]. In contrast, the following PM values were determined in other regions: PM$_{2.5}$/PM$_{10}$ = 23.22 ± 4.72 µg/m$^3$/51.79 ± 12.63 µg/m$^3$ in Mexico City between 2003-2015 [134], 28.4 ± 25.4/87.3 ± 47.3 µg/m$^3$ in Jeddah (Saudi Arabia) [135], 32 ± 6/121 ± 12 µg/m$^3$ in Udaipur, (India) in April 2010 [136], 90/278 µg/m$^3$ in Agra, (India) [137], 21.82/39.45 µg/m$^3$ in Shinjung, (Taiwan) [138], and 38 ± 12/70 ± 31 µg/m$^3$ in townships in South Africa [139].

The PM mass concentrations were observed to be greater during working days (Monday-Saturday) as compared to the weekend day (Sunday) as shown in Table 4.1. Figure 4 also indicates that PM concentrations were low on the four Sundays during November 2016 (i.e., 6, 13, 20 and 27 November). Similar results with reduced PM levels on weekend days have been observed in other parts of the Middle East such as Ahvaz [140] and Tehran (Iran) [140] and Tehran, Iran [141]. This significant difference is due to enhanced anthropogenic activity during working days, including especially vehicular activity and industrial emissions.

**Table 4.1**: 24 hours average PM concentrations during working (Monday-Saturday) and weekend (Sunday) days.

<table>
<thead>
<tr>
<th>Days</th>
<th>PM$_{2.5}$ (µg/m$^3$)</th>
<th>PM$_{10}$ (µg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working</td>
<td>298</td>
<td>671</td>
</tr>
<tr>
<td>Weekend</td>
<td>211</td>
<td>424</td>
</tr>
</tbody>
</table>
Figure 4.3: Daily variation in PM mass concentrations in Peshawar.

4.3 Elemental Composition of PM$_{2.5}$ and PM$_{10}$

Figure 4.4 summarizes the distribution of weight percent of fourteen elements (i.e., O, C, N, Si, Ca, Fe, Al, Cl, K, Mg, S, Na, Ti and Zn) in both PM$_{2.5}$ and PM$_{10}$ based on EDX spectra. Quartz fiber filters consist of Si and O$_2$; therefore, these two elements were subtracted from the loaded filters. The weight percent of O, C, N and Si exceeded those of other elements. The high percentage of C is due to carbonaceous material coming from anthropogenic activities such as vehicular traffic, diesel generators and industrial emissions [142], in addition to biomass burning [143]. One of the major source of Si is soil mineral particles [144]. Therefore, the presence of Si particles in our study is from some likely combination of transported windblown soil particles, re-suspended dust from vehicular traffic or construction and from industrial combustion [145]. Since particulate C offers attractive adsorption sites for various volatile compounds, its higher amount can promote deleterious health effects [146].
4.4 Major Groups of Particulate Matter

On the basis of the PM morphology and chemical structure obtained through SEM – EDX results, sampled particles were classified into the following major groups: Geogenic, Anthropogenic and Biogenic. A discussion of these groups follows subsequently.

4.4.1 Geogenic Particles

Geogenic particles are natural particles that are of crustal origin. They are comprised of quartz, aluminosilicates, calcium-rich particles, chloride-based particles and Fe/Ti oxides.

![Graph of Weight (%) of Various Elements in Peshawar City during November 2016](image)

**Figure 4.4:** The average percent weight of the various elements in Peshawar city during November 2016.

4.4.1.1 Silica/Quartz

The most common name for quartz (SiO₂) particles is silica and they consist of high amounts of Si and O (≈ 50% by weight) [67]. Pure Si particles are produced naturally as well as
artificially [147]. Si is the constituent of sandstone and granite and is the richest chemical component in the Earth’s crust. The basic origin of quartz is soil but it is also found in building materials such as cement, glass, ceramic, bricks and clays. These particles represent 12.3% of the total particles collected (Figure 4.5). The size range of silica is from 2 to 20 µm. In this group, particle types such as like pyrope, grossular, almandine, biotite and fly ash were identified. A triangular shape associated with biotite is shown in Figure 4.6 (b). Fly ash has spherical shape (Figure 4.8 (d)). Pachauri et al. [67] also identified these particles at Agra (India).

![Pie chart showing frequency of particle types observed during the study period.](image)

**Figure 4.5:** Frequency of particle types observed during the study period.

### 4.4.1.2 Aluminosilicates

The major source of aluminosilicates is soil sediments that are present in the highest percentage of the total analyzed Geogenic particles. Therefore, dust is the dominant source of aluminosilicates, while other sources include agricultural activities, fuel combustion and biomass burning [148]. Aluminosilicates account for ~72% of the total chemical compounds in the Earth’s crust [149]. It is evident from our study that aluminosilicate particles obtained from soil are generally composed of Si and Al oxides with varying amounts of Na, K, Mg,
Ca, Fe and Ti. Aluminosilicates represent 23.1% of the total particles collected (Figure 4.5). Their size ranges from 1.2 to 26 µm. In our study, various types of aluminosilicates were identified, including Mg – aluminosilicate (Pyrope), Na-feld spar, K-feld spar, Ca-feldspar, Mg-iron aluminosilicate and Ca-Mg aluminosilicate. Aluminosilicate particles exhibit different shapes and sizes (Figure 4.6 (b-e)): triangular shaped (biotite), trapezium shaped (K-feld spar), soap like (Na-feldspar) and tablet like (Calcium magnesium aluminosilicate). Aluminosilicates have been investigated by others at sites such as Pune (India) [66] and Nigeria [69].
Figure 4.6: SEM-EDX spectra: (a) Blank quartz fiber filter; (b) Biotite, a triangular shaped particle having size of 15.05 µm; (c) K-feld Spar, a trapezium shaped particle having a size of 12 µm; (d) Na-feld spar of shape like soap and size of 26 µm; (e) a tablet shape, calcium-magnesium aluminosilicate of size 2.5 µm.
4.4.1.3 Calcium-Rich Particles

Particles in the calcium-rich group expectedly exhibit a high percentage of Ca, with sources including re-suspended dust, crustal materials from vehicular traffic, construction activities and windblown dust. According to Lough et al. (2005) [150], calcium particles are emitted from construction of roads, houses and buildings. Calcium carbonate particles are a major source of Ca in ambient PM [151]. As shown in Figure 4.7 (a), pentagon shaped carbonate minerals, like Calcite (CaCO$_3$) were identified along with the traces of other soil-related particles. These particles account for 3.1 % of the total analyzed particles (Figure 4.5).

4.4.1.4 Chloride Particles

Chloride particles were present in the form of C-Cl and Na-Cl. Figure 4.7 (b) shows evidence of a particle with tablet-like morphology and a size of 5.6 μm, with traces of C, O, N and Si. These particles account for 1.5 % of the total particles (Figure 4.5). There are other chloride particles such as KCl from biomass burning [152]. Characterization of aerosols at Pune (India) indicated that Cl, Na, Mg and K were soil-derived [153, 154]. Shrivastava et al. [155] noted the presence of chloride particles in aerosols over Delhi (India).

4.4.1.5 Fe/Ti Oxides Particles

This group of particles is assumed to stem from soil emissions. The sources of the high concentrations of Al, Ca, Fe, Mg, Mn, Sr, Ti and Zn are re-suspended road and soil dust [138, 156]. The particles collected from this category were rich in Fe, Ti and O with the combination of mineral dust elements like C, Al, K, Si, Ca, Na and Mg. This group of particles mostly corresponds to Fe oxides with irregular morphology. The particles of this group account for 3.1% of the total particles examined (Figure 4.5). The size range of these particles is from 5.2 to 17.5 μm. A single iron, titanium-oxide particle of spherical morphology having a size of 4.8 μm is shown in Figure 4.7 (c). Similar iron titanium oxide particles of spherical morphology were reported by Pachauri et al. [67] in Agra (India).
Figure 4. 7: SEM-EDX spectra: (a) Ca-rich particle having a size of 17.1 µm with a pentagon-like shape; (b) Chloride particles of size 5.6 µm and tablet-like shape; (c) an iron titanium oxide particle with traces of Ca, K, Mg, Na, Al and Si having size of 4.8 µm and of spherical morphology.
4.4.2 Anthropogenic Particles

Carbonaceous and industrial particles are included in this group of particles. The origin of these anthropogenic particles is local emissions.

4.4.2.1 Carbonaceous Particles

Carbonaceous particles contribute significantly to the total mass of the analyzed samples. The major source of carbonaceous particles in the study site is vehicular emissions. The morphology of these particles ranged from soot to complex structures and depended on different factors such as burning conditions and fuel type [157-159]. Soot is the combination of small individual spheres and has various sources of production like burning of diesels, coal, oil and biomass [160]. A mixture of C-bearing particles and other constituents such as Si, Na, Mg, K, Cl, Ca and Al were also found during the present study. The percentage of these particles is 49 % of the total particles, as shown in Figure 4.5. The particle size varied from 216 nm to 22 µm with variable morphologies. A single C particle with spherical morphology in which the contribution of C and O exceeded 90% is shown in Figure 4.9(a). Earlier research showed that these spherical particles may both scatter and absorb solar radiation [161, 162]. Similar to our results, Pachauri et al. [67] was founded a single carbon particle of completely spherical shape in Agra (India).

Clusters of carbonaceous particles were also observed as shown in Figure 4.8 (b). These particles may also be produced due to agricultural burning and waste incineration [147]. In Peshawar city the peoples uses motorbikes and motorcycles widely which produces Zn in large amount [163]. The extensive use of diesel engines in Peshawar emits high concentrations of C. The congested, slow and jammed traffic in Peshawar produces continuous smoke and soot [2]. In the atmosphere, the major cause of BC is the incomplete combustion of fossil fuels [164].
4.4.2.2 Sulfate particles

In the study site, sulfate particles are produced secondarily from its precursor, SO$_2$ emitted via burning processes. S-related particles are present in all samples of airborne PM [165]. SO$_2$ can be adsorbed on mineral particle surfaces and form secondary minerals [166]. The percentage of sulfate particles was 4.6% of the total particles, as shown in Figure 4.5. The size range of the sulfate particles was from 2.5 µm to 8.4 µm. The sulfate particles also possess capsule-like morphology with sizes on the order of 8.4 µm (Figure 4.8 c).

4.4.3 Biogenic Aerosols

Biogenic aerosols were quantified using methods documented by Matthias-Maser and Jaenicke [167, 168]. Using EDX analysis, morphology and elemental composition were determined. Particles of biological nature, whether dead or alive consisted of slight quantities of Na, Mg, K, P, Si, Fe, Cl, Al and Ca, which are tracers present in plants [168-170]. For the analysis of each biogenic particle, the following clustering method was used as determined by Coz et al. [171]:

Bio aerosol: (C + O) > 75% and 1% < P, K, Cl < 10%

Such particles of biological nature were selected in this group by using the above clustering techniques. Viruses, bacteria, fungal spores, pollen, plant debris and animal matter are included in the biological particles. These particles represent 3.1% of the total particles (Figure 4.5). Single biological particles having spherical shape and size of 4.2 µm are shown in the Figure 4. 8 (e). In these particles of biological nature, C and O are present in major amounts and Na, Mg, K, Ca and Cl were found in smaller amounts. Such types of particles have been reported by many researchers [149, 171-173].
Figure 4.8: SEM-EDX spectra: (a) A spherical carbon particle with C and O (> 90%) having a size of 6.4 µm; (b) A cluster of carbonaceous particle with traces of soil-related elements; (c) A sulfate particle of capsule-like shape having length of 14 µm and width of 2.8 µm; (d) A spherical particle with smooth texture made up of Al-Si-O (fly ash) of size 14 µm; (e) Spherical particles of biological nature having size of 4.2 µm.

4.5 Fourier Transform Infra-Red (FTIR) Spectroscopy

Four loaded samples from PM$_{2.5}$ and three from PM$_{10}$, along with unloaded samples were selected for FTIR analysis from different days. FTIR spectra of both PM$_{2.5}$ and PM$_{10}$ were alike (Figure 4.9). The absorption band at 671 cm$^{-1}$ shows the presence of calcium sulfate (CaSO$_4$) and the absorption band at 713 cm$^{-1}$ indicates the presence of nitrate ions (i.e., NH$_4$NO$_3$) [174]. Si-O bending is located at 800 cm$^{-1}$ for all samples [175]. The band at 880 cm$^{-1}$ is indicative of calcite [176]. Silicate shows its presence at 1040 cm$^{-1}$ (i.e., C-O stretching) [177]. Peaks at 1320 cm$^{-1}$ and 1420 cm$^{-1}$ are indicative of NO$_3^-$ and NO$_4^+$ ions, respectively [178]. The presence of C-C aromatic skeletal stretching is indicated by the peak
at 1620 cm$^{-1}$ and the PM also contains water, which exhibits absorbance at this wavelength [179]. Aldehyde and ketones reveal their presence at the 1700 cm$^{-1}$ band [178]. The peaks at 671 cm$^{-1}$ and 2111 cm$^{-1}$ represent CO$_2$ and CO, respectively, which suggests that the evaporative fraction contains organic and elemental C [179]. The peaks at 2850 cm$^{-1}$, 2920 cm$^{-1}$, 3030 cm$^{-1}$, 3400 cm$^{-1}$ are the clear indication of aliphatic C-H stretching, aliphatic C-H stretching, aromatic C-H stretching and O-H stretching absorbance [177].

Figure 4. 9: FTIR spectrum of (a) PM$_{2.5}$ (b) PM$_{10}$ collected at Peshawar during November 2016.

4.6 Identification of Aerosol Sources

Based on SEM-EDX and FT-IR analysis, the following sources of aerosols were identified, which contributed to the aerosol loading over Peshawar:

4.6.1 Combustion Sources (Vehicular Emissions/ Biomass Burning)

In this work, the carbonaceous particles were found to be the most abundant. Since sampling was carried out near a roadside and railway tracks, the main source of carbonaceous particles was vehicular and industrial emissions. Biomass burning is the other source because in autumn season biomass burning is common in the region. Soot particles produced from the combustion process, so its cause is the vehicular traffic. Sulfur particles (S) were also found
in the current study. Generally sulfur produce from the fuel burning and set down on the existing minerals [66]. Similarly, Fe/Ti oxides were also found in the current work. The particles contained high amounts of Fe in the form of oxides and alloys, accompanied by metals (Cu, Zn, K, Pb, Ni and Cr), which produce from traffic and industrial sources [180].

4.6.2 Soil dust/Re-Suspension of Road Dust
In the present study, aluminosilicates were found in the highest amount after the carbonaceous particles. Likewise, chloride particles were also found in the form of C-Cl and Na-Cl. Re-suspended road and soil dust are the main sources of the great concentrations of Al, Ca, Fe, Mg, Mn, Sr, Ti and Zn [138]. Kulshrestha et al. [153] and Parmar et al. [154] characterized aerosols at Pune (India) and reported that Cl, Na, Mg and K stemmed from soil in their analyzed samples.

4.6.3 Cement/Limestone
In the current study Ca-rich particles were present as CaCO$_3$ (limestone) with other elements like Al, K, Zn, Cu and Si. According to Lough et al. [150], calcium particles are emitted from construction of roads, houses and buildings. Due to construction activities and re-suspended dust in the vicinity of sampling site, Ca-rich particles were found in the present study.

4.6.4 Biological Particles
In the present research work these particles were also studied. The sources of these particles are viruses, bacteria, fungal spores, pollen, plant debris and animal matter. The sampling site was surrounded by a large number of plants, trees and agricultural land.
Chapter 5

Temporal Characteristics of the Optical Properties of Aerosol at the Glacier Location (Northern Pakistan): Implications for Climate Forcing

5.1 Local Meteorological Conditions

The data of meteorology was provided by the department of meteorology (Gilgit-Baltistan). The meteorological situation in Gilgit, Skardu and Diamer is summarized in Figure 5.1 (a-d). In Gilgit, Skardu and Diamer, maximum rainfall (RF) accumulation of 18.94, 31.24 and 25.59 mm was recorded, respectively, during spring months. In Gilgit, the minimum RF of 7.44 mm was observed during winter, while in Skardu and Diamer exhibited minimum RF of 9.64 and 6.10 mm, respectively, during autumn months. Maximum relative humidity (RH) values at Diamer and Skardu were found to be 56.38 %, 56.38 % and 81.59 %, respectively, during winter, while in Gilgit it was 77.60 % both in winter and autumn. Maximum temperatures were observed during the summer with values of 34.93 °C (Gilgit), 30.42 °C (Skardu) and 37.64 °C (Diamer). Wind speed varied from 0.1 to 2.1 ms\(^{-1}\), 0.1 to 2.4 ms\(^{-1}\) and 0.1 to 3.9 ms\(^{-1}\) in Gilgit, Skardu and Diamer, respectively, with corresponding averaged wind speeds of 0.54, 0.61 and 1.29 m s\(^{-1}\). In Gilgit and Diamer, the winds were predominantly westerly while in Skardu the winds were mainly south easterly and north westerly.
(a) RF - RH - Min Temp - Max Temp

Gilgit
Skardu
Diamer

(b) Flow Vector Wind

Calms: 0

m/s

- 2.2
- 2.2
1.8 - 2
1.6 - 1.8
1.4 - 1.6
1.2 - 1.4
1.0 - 1.2
0.8 - 1.0
0.6 - 0.8
0.4 - 0.6
0.2 - 0.4
0 - 0.2
Figure 5. 1: (a-d): Prevailing meteorological conditions of Gilgit, Skardu and Diamer from 2004 to 2016.
5.2 Variation in Optical Properties of Aerosol

5.2.1 Aerosol Optical Depth

In current research study, the seasonal and monthly variations in AOD values were analyzed with OMI data at 500 nm for the period between 2004 and 2016. Figure 5.2 (a-b) shows the seasonal and monthly variations in AOD. The AOD values were higher during spring, followed by summer, autumn and winter. During spring and summer, the AOD values ranged from 0.49 to 0.67 and 0.49 to 0.65, respectively. Similarly, the AOD value for autumn and winter varied between 0.27 to 0.43 and 0.22 to 0.33, respectively. For the whole area, the highest AOD of 0.65 ± 0.11 was observed during May and the lowest value of 0.24 ± 0.04 was noted during December.

Table 5.1: Seasonal average variation in AOD, AI, AAOD and SSA with the corresponding standard deviation (STD) over the study area for the period between 2004 and 2016.

<table>
<thead>
<tr>
<th>Region</th>
<th>Seasons</th>
<th>AOD±STD</th>
<th>AI ± STD</th>
<th>AAOD ± STD</th>
<th>SSA ± STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gilgit</td>
<td>Spring</td>
<td>0.53 ± 0.05</td>
<td>0.78 ± 0.19</td>
<td>0.01 ± 0.005</td>
<td>0.98 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.45 ± 0.03</td>
<td>0.77 ± 0.23</td>
<td>0.02 ± 0.002</td>
<td>0.96 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.31 ± 0.06</td>
<td>0.75 ± 0.21</td>
<td>0.01 ± 0.004</td>
<td>0.96 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>0.32 ± 0.07</td>
<td>0.81 ± 0.34</td>
<td>0.01 ± 0.003</td>
<td>0.96 ± 0.03</td>
</tr>
<tr>
<td>Skardu</td>
<td>Spring</td>
<td>0.66 ± 0.15</td>
<td>0.75 ± 0.06</td>
<td>0.01 ± 0.07</td>
<td>0.98 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.50 ± 0.06</td>
<td>0.78 ± 0.07</td>
<td>0.02 ± 0.003</td>
<td>0.96 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.38 ± 0.07</td>
<td>0.85 ± 0.62</td>
<td>0.02 ± 0.005</td>
<td>0.96 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>0.32 ± 0.01</td>
<td>0.81 ± 0.53</td>
<td>0.006 ± 0.002</td>
<td>0.97 ± 0.01</td>
</tr>
<tr>
<td>Diamir</td>
<td>Spring</td>
<td>0.46 ± 0.06</td>
<td>0.76 ± 0.15</td>
<td>0.02 ± 0.004</td>
<td>0.96 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.44 ± 0.05</td>
<td>0.68 ± 0.1</td>
<td>0.02 ± 0.003</td>
<td>0.96 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.27 ± 0.03</td>
<td>0.80 ± 0.34</td>
<td>0.01 ± 0.003</td>
<td>0.95 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>0.26 ± 0.04</td>
<td>0.95 ± 0.54</td>
<td>0.01 ± 0.005</td>
<td>0.96 ± 0.01</td>
</tr>
<tr>
<td>Whole</td>
<td>Spring</td>
<td>0.60 ± 0.06</td>
<td>0.72 ± 0.06</td>
<td>0.017 ± 0.004</td>
<td>0.97 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.57 ± 0.06</td>
<td>0.71 ± 0.04</td>
<td>0.020 ± 0.004</td>
<td>0.96 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.34 ± 0.05</td>
<td>0.68 ± 0.09</td>
<td>0.015 ± 0.003</td>
<td>0.95 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>0.28 ± 0.04</td>
<td>0.78 ± 0.2</td>
<td>0.009 ± 0.004</td>
<td>0.97 ± 0.01</td>
</tr>
</tbody>
</table>

STD = Standard Deviation

Table 5.1 summarizes how AOD characteristics vary in all three locations of the Gilgit-Baltistan province relative to the entire study region for each season. In Gilgit, AOD in spring, summer, autumn and winter seasons ranged from 0.44 – 0.62, 0.40 – 0.50, 0.23 – 0.44 and 0.18 – 0.38, respectively. In Skardu, the values of AOD varied from 0.35 – 0.90,
0.43 − 0.61, 0.31 − 0.52 and 0.18 − 0.49 during the four seasons. The range of AOD for Diamer were found from 0.40 − 0.60, 0.37 − 0.52, 0.22 − 0.33 and 0.21 − 0.32 for the above four seasons. During spring, the maximum AOD value is largely due to vehicular emissions, biomass burning, local pollutants and strong wind erosion leading to dust over glacier region. High AOD during spring is also due to long-range transport of dust brought by westerly winds from different regions like Sahara and Thar Deserts, West Asia and Middle East; those air masses pass mostly above the IGP plain and reached the Himalayas region [181-183]. In spring, due to the higher convection and abrupt pressure gradient, dust-rich aerosols reach high-elevated stations along the slopes of the Himalayas [184]. Mineral dust carried from deserts through long-range transportation is responsible for the significant increase in AOD at Manora Peak (central Himalaya) [87]. High AOD may also be due to dust transported from nearest Cold Desert (Katpana Desert) in the region.

The enhanced fire activities in the pre-monsoon (spring) increases the AOD value over North-East India. Chatterjee et al. [185] also reported maximum values of AOD in spring over Darleging, Eastern Himalaya. The reason for higher AOD over Darleging in the spring season is due to dry lands, which lead to increase in the solar heating rate causing dust to rise from various regions (arid and semi-arid). During spring and summer season, dust is the main contributor to the increased AOD than other types of aerosols over the Tibetan plateau [186]. Lower values of AOD observed in winter and autumn are because of the existence of anthropogenic aerosols and the high washout process that occur due to heavy rains in most sites over glacier region, which removes aerosols from the environment [187, 188].
5.2.2 Ultraviolet Aerosol Index

Seasonal and monthly variations in AI values over the whole region are given in Figure 5.3 (a-b). During the four seasons, the AI values ranged from 0.60 − 1.28, 0.64 − 0.87, 0.64 − 0.78 and 0.58 − 0.90, respectively. For the whole area, the highest (0.86 ± 0.34) and lowest (0.64 ± 0.07) AI values were observed during January and October, respectively. Significant seasonal variations in AI were also investigated over Gilgit, Skardu and Diamer (Table 1). Over Gilgit, AI values ranged from 0.59 − 1.11 and from 0.52 − 1.22 during spring and summer seasons, respectively. Similarly, during autumn and winter seasons, the values of AI were found to vary from 0.53 − 1.14 and from 0.58 − 1.49, respectively. Over Skardu, the AI values during four season ranged from 0.67 − 0.83, 0.70 − 0.90, 0.57 − 2.76 and 0.50 − 2.21, respectively. For Diamer, AI values during spring, summer, autumn and winter varied from 0.54 −1.11, 0.52 − 0.86, 0.57 − 1.75 and 0.63 − 2.48, respectively. Table 1 shows the seasonal average values of AI for the study region. No negative value of AI was obtained over the study area, which indicates the domination of Ultraviolet absorbing aerosols. However, at North Greece, Kaskaoutis et al. [189] reported negative values of AI during summer, indicating the dominance of scattering aerosols (coarse particles).
The AI variations were linked with the seasonal variations in dust, smoke, rainfall and burning activities in the area. The absorbing aerosols in winter season are mostly fine particles [101], which arise due to burning of woods, dung and other fuels [190]. During the autumn months, increase in temperature, wind speed and dust storm activities promote enhanced AI values. In summer, due to the unstable atmospheric conditions, aerosol are lifted to greater height, which results in less AI values as compared to other seasons [101, 191]. Chatterjee et al. [185] reported that high values of AI during spring over Himalaya stem from wind-blown dust driven by westerlies. Sreekanth et al. [192] reported high AI (spring) and low AI (winter) over the northwestern part of Bay of Bengal.

![Box-whisker plots indicating (a) seasonal variations in AI at the whole study site (b) monthly variation in AI over the entire study region.](image)

**Figure 5.3**: Box-whisker plots indicating (a) seasonal variations in AI at the whole study site (b) monthly variation in AI over the entire study region.

### 5.2.3 Absorbing Aerosol Optical Depth

The seasonal and monthly variation in AAOD over the whole region is shown in Figure 5.4 (a-b). The maximum AAOD was found in summer and a minimum in winter season. During spring, summer, autumn and winter, AAOD values ranged from 0.013 – 0.028, 0.017 – 0.024, 0.010 – 0.017 and 0.005 – 0.019, respectively. For the whole area, the highest monthly mean AAOD (0.02 ± 0.007) was found during April and the lowest (0.006 ± 0.005) was observed during February.
Over Gilgit, during spring, summer, autumn and winter, AAOD values ranged from 0.004 – 0.02, 0.01 – 0.020, 007 – 0.020 and 005 – 0.04, respectively (Table 1). Over Skardu, AAOD during the above four seasons, varied from 0.002 – 0.03, 0.013 – 0.02, 0.01 – 0.03 and 0.003 – 0.009. Similarly, the AAOD values over Diamer during the four seasons ranged from 0.01 – 0.02, 0.01 – 0.03, 0.008 – 0.02 and 0.006 – 0.02, respectively.

AAOD indicates the absorbing nature of aerosols, where BC and dust are the prominent contributors [101], consistent with the sources impacting the study region. Vadrevu et al. [193] reported AAOD values of 0.075 and 0.05 during summer and winter seasons, respectively, over Punjab (India). In a study carried out by Torres et al. [117] over central Africa, which was based on five-year period, the maximum AAOD values obtained were in the range from 0.08 – 0.12 during August. They also documented the monthly variations in AAOD from 0.08 to 0.15 in the month of September over South America. Bibi et al. [101] noted that over Karachi, the AAOD varied from 0.01 – 0.065. Enhanced dust loading is responsible for the high value of AAOD, whereas less contribution of coarse particles is attributed for low values of AAOD in winter [194].

![Figure 5.4](image)

**Figure 5.4:** Box-whisker plots indicating (a) seasonal variations in AAOD over the entire study region (b) monthly variation in AAOD over the entire study region.
5.2.4 Single Scattering Albedo

Figure 5.5 (a-b) represents the seasonal and monthly variation in SSA for the whole region. The values of SSA ranged between 0.96 – 0.98, 0.96 – 0.97, 0.95 – 0.96 and 0.94 – 0.98 during the four seasons, respectively. The maximum average SSA was observed in February (0.98 ± 0.004) and the minimum SSA was observed in October (0.96 ± 0.003) over the whole region. Table 1 shows the average values of SSA in Gilgit, Skardu and Diamer. For Gilgit, during the four seasons the SSA ranged from 0.97 – 0.99, 0.96 – 0.97, 0.95 – 0.97 and 0.87 – 0.99, respectively. For Skardu, the SSA values obtained during four seasons ranged from 0.96 – 0.99, 0.95 – 0.97, 0.94 – 0.97 and 0.94 – 0.98, respectively. SSA values over Diamer during the four seasons ranged from 0.94 – 0.98, 0.95 – 0.96, 0.93 – 0.97 and 0.93 – 0.98, respectively.

SSA values are high during winter because of the existence of a diverse mixture of anthropogenic sources (fossil fuel combustion, organic aerosols and absorbing soot), while during summer and spring, high values may be attributed to dust-derived coarse particles. During autumn, SSA values were slightly lower than other seasons, suggesting that dust is not a main source but local fine aerosol particles are relatively more important. High values of SSA in spring are also due to high temperatures and wind speeds, which lifts loose soil particles. The high values of SSA during the summer are because of the presence of more water-soluble particles in the atmosphere and the dust aerosols (coarse particles). During pre-monsoon (spring) and monsoon seasons, enhanced water vapor levels are present in the atmosphere and particles swell owing to both hygroscopic growth and heterogeneous chemistry, resulting in greater SSA values at higher wavelengths [183]. Desert dust transport events over India and China can significantly change SSA values ranging from 0.75 – 0.99 [195].
Pant et al. [98] reported the SSA over Monora Peak ranged between 0.87 − 0.94 (Average 0.90) in winter season. Over the Himalayan range (Nepal), Ramana et al. [88] reported the value of SSA (0.7 − 0.9) in the winter season (2004). Gautam et al. [86] reported that for the period of spring season, SSA values along with standard deviations at different sites along the Himalayan foothills (i.e., Hetauda, Dhulikhel and Langtang) were 0.86 ± 0.02, 0.88 ± 0.02 and 0.89 ± 0.03, respectively, at a wavelength of 441 nm. Mareq et al. [79] reported that during spring, SSA varied from 0.82 to 0.89 at the Nepal Climate Observatory-Pyramid. Weller et al. [196] noted the SSA values at 550 nm over the Antarctica ranged from 0.95 - 1.00 with an average value of 0.99 ± 0.009. Nair et al. [197] noted SSA values of 0.97 and 0.96 over Himalayan stations like Hanle during pre-monsoon and winter seasons. Ramanathan et al. [198] obtained SSA values of the range from 0.95 - 0.99 over the Southern Indian Ocean; our calculated values of SSA are comparable to those values.

![Figure 5.5](image)

**Figure 5.5**: Box-whisker plots indicating (a) seasonal variations in SSA over the whole region (b) monthly variations in SSA over whole region.

5.3 Frequency Distribution of Seasonal AOD, AI, AAOD and SSA

In Figure 5.6, variations in AOD, AI, AAOD and SSA are summarized using a histogram format. In each plot, the number of observed days and seasonal average values with associated standard deviations are given for each parameter. For each season, a large
difference in the distributions for each parameter was noted, signifying the considerable seasonal heterogeneity. The analysis of frequency distribution shows that AOD $> 0.6$ accounted for 75% of data during the summer, 68% during spring, 14% during autumn and 8% during winter suggestive of high aerosol loading during summer and spring. The frequency of AI $> 0.5$ was 100% during all the four seasons, confirming the existence of absorbing aerosols in all seasons. AAOD frequency was observed to be highest in summer (84%) followed by autumn (69%), spring (68%) and winter (42%). The maximum value of AAOD during summer is due to high absorption of coarse particles at lower wavelengths. Likewise, the highest frequency of SSA values equal to 1 was noted during winter (69%), followed by spring (61%), autumn (42%) and summer (37%). The highest AI value in winter season is the indication of a mixture of anthropogenic aerosols. Recently, Tiwari et al. [81] also reported the same type of frequency distribution for New Delhi, India, they further noted that during the four seasons, the large variations in AOD shows various particle classes produced by diverse emission sources.
Figure 5.6: Seasonal frequency distributions (%) AOD, AI, AAOD and SSA. N represents number of observed days and m indicate seasonal mean, over the study region between 2004 and 2016.
5.4 Trend Analysis of Seasonal AOD, AI, AAOD and SSA

Inter-annual variations in optical parameters (AOD, AI, AAOD and SSA) are summarized in Figure 5.7 (a-d) over the study region between 2004 and 2016. To calculate the slope, intercept and trend, a linear regression method is used [199]. AOD exhibits an increasing tendency (0.006 yr\(^{-1}\)), with the lowest and highest values of 0.21 and 0.61 observed in winter 2010 and summer 2016, respectively, with an overall average of 0.44 ± 0.15. An increasing trend for AI (0.005 yr\(^{-1}\)) was noted over the study region. The lowest seasonal AI (0.57) was noted in autumn 2004 and the maximum seasonal AI (1.27) was observed in winter 2016 with an overall average value of 0.72 ± 0.12. An increasing trend of AAOD (0.0001 yr\(^{-1}\)) was also noted over the region. The minimum AAOD value of 0.005 was observed in winter 2007 and the maximum value of 0.28 was observed in spring 2014, with an overall average of 0.015 ± 0.004. A decreasing trend of SSA (-0.0002 yr\(^{-1}\)) was noted over the study region. The minimum SSA (0.94) was found in autumn 2016 and the maximum value of 0.98 was observed in winter 2004, the overall average was 0.96 ± 0.12. The relatively small SSA shows the dominance of absorbing aerosol. All the trend results show the increasing amount of aerosols (absorbing), which confirms the presence of absorbing aerosols, although the types of these aerosols differs seasonally. Alam et al. [1] noted the increasing tendency for AI over ten selected locations in Pakistan. Similarly Tariq et al. [191] also pointed out the increasing trend for AI over Pakistan.

This increasing trend in aerosol, especially those of a light-absorbing nature, over the glacier region significantly heat up the atmosphere. Furthermore, the deposition of these absorbing particles on snow/ice surfaces enhances glacier melt. Consequently, a catastrophic situation is projected for the study region, with flooding being one of many negative outcomes.
5.5 Aerosol Radiative Forcing and Atmospheric Heating Rate

Aerosol Radiative Forcing (ARF) is calculated from incoming and outgoing fluxes, as obtained from CERES data. The seasonal average variations in ARF with associated Atmospheric Heating Rate (AHR) at the TOA, SRF and within Atmosphere (ATM) are shown in Figure 5.8, while average radiative forcing at TOP, SRF and within ATM are summarized in Table 5.2. The observed ARF were noted to be negative at the TOP and at the
SRF, whereas within ATM, its value was found to be positive. From Figure 5.8, it is clear that the ARF at the TOA and SRF having a clear difference, owing to radiation absorbed within the atmosphere resulting in Atmospheric Heating, which subsequently can decrease eddy heat convergence and surface temperature [200, 201].

**Table 5.2:** Average ARF at the TOP, SRF and within ATM.

<table>
<thead>
<tr>
<th>Seasons</th>
<th>Radiative Forcing (W m(^{-2})) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOP</td>
</tr>
<tr>
<td>Spring</td>
<td>-13.25 ± 11.81</td>
</tr>
<tr>
<td>Summer</td>
<td>-37.75 ± 15.78</td>
</tr>
<tr>
<td>Winter</td>
<td>-7.16 ± 6.47</td>
</tr>
</tbody>
</table>

SD = Standard Deviation

The maximum radiative forcing was observed in the summer followed by spring, autumn and winter season. The radiative forcing value in summer was high due to the dominance of coarse particles, which efficiently absorbed incoming solar radiation, leading to atmospheric heating.

Radiative forcing values obtained at the TOP during spring, summer, autumn and winter ranged from -42.42 to 2.90 W m\(^{-2}\), -68.73 to -6.12 Wm\(^{-2}\), -55.37 to 11.88 Wm\(^{-2}\) and -22.75 to 3.05 Wm\(^{-2}\), respectively. ARF observed at the surface in spring, summer, autumn and winter varied between -95.68 and -33.33 Wm\(^{-2}\), -130.20 and -51.08 Wm\(^{-2}\), -91.85 and -15.24 Wm\(^{-2}\) and -65.15 and -22.11 Wm\(^{-2}\), respectively. However, the radiative forcing within ATM were found to range from 33.57 to 62.54 Wm\(^{-2}\), 42.09 to 74.36 Wm\(^{-2}\), 18.72 to 45.22 Wm\(^{-2}\) and 21.85 to 45.19 Wm\(^{-2}\) during four seasons, respectively.

Zhang et al. [50] documented that over the entire Tibetan Plateau, the annual mean ARF at SRF was 0.42 Wm\(^{-2}\) (BC) and 0.33 Wm\(^{-2}\) (dust), respectively, with a high value in spring. Qu et al. [202] reported that the ARF due to dust and BC were 2.7 ± 3.4 W m\(^{-2}\) and
4.8 ± 3.2 W m\(^{-2}\), respectively, over Zhadang glaciers during summer 2012. During spring, Quin et al. [203] reported that due to aerosols, the resulting perturbation in snow albedo caused a surface radiative flux change from 5 to 25 W m\(^{-2}\). Kumar et al. [53] reported surface variations of radiative forcing between -26 and -53 W m\(^{-2}\) at Nainital (north India) during the spring season. The TOA, SRF and within ATM radiative forcing values reported by Dumka et al. [85] over Nainital were -7.61, -45.75 and 38.14 Wm\(^{-2}\), respectively. Similarly, Lau and Kim [10] reported the values of ARF at the TOP, SRF and within ATM to be -4.5, -21.3 and 16.8 W m\(^{-2}\), respectively, over the Tibetan Plateau. Ramana et al. [88] found the ARF at TOA, SRF and within ATM over Kathmandu to be -0.2, -25 and 25 Wm\(^{-2}\), respectively.

According to Prasad and Singh [204], for the dust period that occurred in April-May 2005, the SRF and TOA radiative forcing varied from -19 to -87 Wm\(^{-2}\) and from 2 to -26 Wm\(^{-2}\), respectively, which are comparable to our observations. Mareq et al. [79] also showed that radiative forcing at SRF ranged from -1.6 to -19 Wm\(^{-2}\) during spring at Nepal Climate Observatory-Pyramid.

The average atmospheric HR during spring, summer, autumn and winter was 1.28, 1.52, 0.89 and 0.88 °K day\(^{-1}\), respectively (Figure 12). The high heating rates in summer and spring indicate great atmospheric absorption. In summer season, usually absorbing dust combines with black carbon aerosols, while during winter season, absorbing black carbon exhibits high concentrations causing high HR [205].
Figure 5.8: Seasonal variations in radiative forcing with the corresponding values of (HR) for four seasons (HR values written in parenthesis).

5.6 Satellite Monitoring and Aerosol Transport Over Glacier Region

Figure 5.9 shows the various transects of CALIPSO across the glacier study region for different seasons. The Figure 5.9 depicts the consistent presence of BC, sulfate and biomass burning, with low values of VDR during autumn and winter. The presence of coarse dust particles during spring and summer is supported by VDR values exceeding 0.5 during spring and summer. These results were further verified and modified by analysing aerosol sub-type observations.
Figure 5.9: Volume depolarization ratio (VDR) values for CALIPSO transects across the glacier region during four seasons.
The aerosol sub-type profiles obtained from CALIPSO during summer, spring, autumn and winter are presented in Figure 5.10. During summer and spring, the prominent aerosol types are dust and polluted dust (coarse particles), which reached an altitude of 10 km over study site. Dust aerosols were present due to long-range transport and polluted dust ascribed to anthropogenic events [206]. CALIPSO observations also showed that polluted dust and smoke (fine particles) were the dominant aerosol sub-types during winter, which extended up to a 7 km. During autumn, the aerosol layer stretched up to 7 km, with smoke (fine particles) being most important with seldom influence from polluted dust (coarse particles). Cong et al. [207] also observed a thick layer of aerosols over the Himalaya and Tibetan plateau reaching over 6 km by using the CALIPSO retrieved aerosol sub-type information for 17 April 2010.
Figure 5.10: Aerosol classification by CALIPSO.

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model is useful to find the origin of air masses affecting a receptor site [122]. This model has been used to find out the mean aerosol transport pathways from the various surrounding regions to the study site at 1000 m above the ground (Figure 5.11). These trajectories are representative of the four seasons. During spring, 62.5% of air masses come from the Dasht Desert (Iran), 12.5% from Saratgard and Rajasthan (India) and 25% from central Punjab mainly Cholistan Desert (Pakistan). During summer, 64.3% of air masses come from Turkmenistan, 28.6% from Peshawar (Pakistan), while 7.1% are of local origin. Overall, the maximum contribution of long-range transported aerosols was noted during spring and summer, which confirms the existence of coarse particles over the study region. During autumn, 25% of air masses come from Faisalabad (Pakistan), which pass through Amritsar (India) before reaching the receptor site, 12.5% come from Tajikistan and Afghanistan and 62.5% are of local origin. During winter, 80% of air masses come from Sialkot (Pakistan) and Shakargard
(India), 13.3 % from Azerbaijan and 6.7 % from Loristan province (Iran). Thus, during autumn and winter, the trajectories were mostly local leading to great contribution by fine particles as compared to coarse particles over the study region. These results were in agreement with CALIPSO retrievals. To explore aerosol sources and their possible pathways, similar cluster trajectories were examined previously in other regions [9, 101].

Figure 5. 11: Three-day air mass back trajectories ending at the receptor site for the four seasons, with different colors representing percentage of air masses.
Chapter 6
Spatio-Temporal Variations of Black Carbon and its Relationship with Meteorology over Four High Altitude Sites in Glaciated Region of Pakistan

6.1 Meteorological Conditions

The meteorological data used in this work was obtained by the expedition team using Automatic Weather Stations installed temporarily at each site during the monitoring. Figure 6.1 (a, b) indicated the daily average surface meteorology parameters. The maximum average Temp, RH, RF and WS were reported to be 20.3 °C (Skardu), 47.9 % (Skardu), 5 mm (Sost) and 3.9 m/s (Sost) during June, December, June and December, respectively. Minimum values of the Temp, RH, RF and WS were found to be 1.3 °C (Skardu), 20.7 % (Astore), 0.1 mm (Skardu), 1.2 m/s (Gilgit) during December, May, June and May, respectively. According to Roy et al. [208], Particulate Matter (PM) has different sources which vary with place, season and weather condition. During the recent years the decreasing trend has been observed in temperature, which is due to the rising concentration of PM in the atmosphere [67]. The highest concentration of PM has been noted by various researchers during stable meteorological conditions (low wind speed, inversion) [209]. Pant et al. [98] found that over Monora Peak the wind speed ranged from 2 to 4 m/s, Temp varies from 8 to 15 °C and RH ranged from 50 to 70 % during December 2004.
Figure 6. 1: Daily variations in RF, Temp, RH and WS over four high altitude stations between (a) May-June (b) November-December 2016.

6.2 Daily Variation in BC Mass Concentration

The BC variations were determined on a daily basis during the months of May, June, November and December (2016). BC mass concentration exhibited strong daily variations during the study period. At Astore, Gilgit and Sost, during May, the BC mass concentration
varied from 2.3 to 2.9, 2.1 to 4.7 and 0.9 to 1.6 µg/m³, respectively. The BC concentration during June varied from 2.6 − 4.1 µg/m³ at Sost. Similarly, in November, at Astore and Gilgit, the mass concentration of BC ranged from 2.5 − 3.7 and 3.5 − 4.7 µg/m³, respectively. During December at Gilgit, Sost and Skardu, the BC mass concentration varied from 2.8 − 6.1, 1.5 − 2.7 and 3.2 − 4.7 µg/m³, respectively. During May and June, the highest BC concentration of 4.7 µg/m³ occurred on 19 May at Gilgit, while a minimum concentration of 0.9 µg/m³ occurred on 28 May at Sost (Figure 6.2 (a, b). During November and December, the highest concentration of BC was found to be 6.1 µg/m³ on 1 December at Gilgit, while the lowest BC concentration of 1.5 µg/m³ was observed on 12 December at Sost (Figure 6.2 (a, b). During the whole period, the highest BC mass concentration of 6.1 µg/m³ occurred at Gilgit (1 December) and the lowest concentration of 0.95 µg/m³ occurred at Sost (28 May), as presented in the Figure 6.2 (a, b). Zero RF, low WS and RH and relatively high Temp is responsible for high BC concentration on 1 December.
Figure 6.2: Daily average variation in BC mass concentration over Astore, Gilgit, Sost and Skardu in northern Pakistan between (a) May-June (b) November-December 2016.

6.3 Monthly Variation in BC Concentration

The monthly average temporal difference in BC concentration is given in Figure 6.3. During the month of May the value of BC at Astore, Gilgit and Sost ranged from 2.3 – 2.9 µg/m$^3$ (Average 2.6 ± 0.2 µg/m$^3$), 2.1 – 4.7 µg/m$^3$ (Average 3.5 ± 0.6 µg/m$^3$) and 0.9 – 1.6 µg/m$^3$ (Average 1.2 ± 0.2 µg/m$^3$), respectively. During June, BC levels at Skardu and Sost ranged from 2.6 – 4.1 µg/m$^3$ (Average 3.0 ± 0.5 µg/m$^3$) and 0.4 – 1.6 µg/m$^3$ (Average 0.9 ± 0.3 µg/m$^3$), respectively. During November at Astore and Gilgit the value of BC ranged from 2.5 – 3.7 µg/m$^3$ and 3.5 – 4.7 µg/m$^3$ with corresponding average (3.3 ± 0.4 µg/m$^3$ and 4.1 ± 0.4 µg/m$^3$), respectively. Similarly, during December at Gilgit, Sost and Skardu the values of BC varied from 3.5 – 4.7 µg/m$^3$, 1.5 – 2.7 µg/m$^3$ and 3.2 – 4.7 µg/m$^3$, with corresponding average values of 4.1 ± 0.4 µg/m$^3$, 2.2 ± 0.5 µg/m$^3$ and 3.9 ± 0.6 µg/m$^3$, respectively. The maximum BC mass concentration of 4.1 ± 0.4 µg/m$^3$ was reported in the month of November as well as in December at Gilgit and the minimum BC (0.9 µg/m$^3$) was noted in June at Sost.
The average BC concentration over all locations was noted to be $3.1 \pm 1.1 \, \mu g/m^3$. The average BC was higher in November and December months as compared to May and June.

The BC mass concentration of $1.3 \pm 0.9 \, \mu g/m^3$ at Monora Peak during December 2004 was found by Pant et al. [98]. Raju et al. [94] reported BC concentrations of $0.6 \pm 0.6 \, \mu g/m^3$ and $0.9 \pm 0.2 \, \mu g/m^3$ during May and December, respectively, over an Indian high altitude location (Sinhagad); those values are also less than ours. Safai et al. [96] also found high BC concentrations during November and December with minimum values in May and June at the coastal urban city of Pune (India). Bibi et al. [101] also reported a high BC concentration of $7.5 \, \mu g/m^3$ (December) and a low concentration of $2.9 \, \mu g/m^3$ (June) during 2007 over Karachi. Over Karachi during 2006 to 2007, Dutkiewicz et al. [123] also found higher BC value of $10 \, \mu g/m^3$ (November – February) and lower value of $2 \, \mu g/m^3$ (June – September). Ramachandran and Kedia [127] noted the maximum monthly average BC value of $13.8 \, \mu g/m^3$ during December and minimum concentration of $1.6 \, \mu g/m^3$ during June over Ahmadabad (India). Likewise, Kalluri et al. [102] observed the maximum BC mass concentration of $3.4 \pm 1.2 \, \mu g/m^3$ in January and the lowest concentration of $1.1 \pm 0.2 \, \mu g/m^3$ in July over Anantapur (India).
6.4 Diurnal Variation in BC Concentrations: Effect of Anthropogenic Activities, Mountain and Valley Wind

Figure 6.4 shows the hourly average BC variations for the whole study duration. During the month of May at Astore, Gilgit and Sost, the sharp morning peak appeared at 10:00 LST (3.7 µg/m³), 11:00 LST (4.3 µg/m³) and 08:00 LST (2.0 µg/m³), respectively. Likewise, at Gilgit the evening peak appeared at 18:00 LST (4.6 µg/m³) and at Astore and Sost, they appeared at 20:00 LST with BC concentrations of 4.0 µg/m³ and 1.8 µg/m³, respectively. At Sost and Skardu during June, BC mass concentration started to increase at the same time (i.e., from 04:00 LST) and attained a morning peak at 09:00 LST (1.7 µg/m³) and 10:00 LST (4.5 µg/m³), respectively, followed by a subsequent decrease. Similarly, an evening peak emerged at 20:00 LST (1.8 µg/m³) and 21:00 LST (4.6 µg/m³), after which BC concentration decreased. During November at Astore and Gilgit, BC started to increase after 07:00 LST with a peak at 10:00 LST (3.9 µg/m³) and 12:00 LST (4.8 µg/m³), respectively. Likewise, the
evening peak appeared at the same time (i.e., 23:00 LST) with BC concentrations of 4.3 µg/m³ and 5.5 µg/m³, respectively. During December at Gilgit, Sost and Skardu, the morning peak appeared at 05:00 LST (5 µg/m³), 09:00 LST (10.5 µg/m³) and 10:00 LST (5.9 µg/m³), respectively and then declined. Likewise, evening maxima came into view at 23:00 LST (5.5 µg/m³), 20:00 LST (4.0 µg/m³) and 19:00 LST (6.5 µg/m³), respectively.

Figure 6. 4: Diurnal variation in BC concentration during May, June, November and December at Astore, Gilgit, Sost and Skardu.

The monthly variation in the ratio of the day/night (06:00 − 18:00) / (18:00 − 06:00) in BC concentration is shown in the Figure 6.5. During May at Astore, Gilgit and Sost, the day/night ratios of BC were found to be 0.8, 1.1 and 0.7, respectively. During June at Sost and Skardu, the day/night ratios were 0.7 and 1.1, respectively. Similarly, during November at Astore and Gilgit, the day/night ratios were 0.7 and 0.8, respectively. During December at
Gilgit, Sost and Skardu, the day/night time ratios were 0.8, 1.8 and 1.1, respectively.

![Graph showing day/night time BC concentration ratio at the study sites during 2016.](image)

**Figure 6.5**: Day/night time BC concentration ratio at the study sites during 2016.

Higher day time BC concentrations during May (Gilgit), June (Skardu) and December (Skardu, Sost) were due to the dominance of sources during daytime such as vehicular emissions, agriculture and biomass burning activities. Likewise, the high nighttime BC concentrations during May (Astore and Sost), June (Sost), November (Astor and Gilgit) and December (Gilgit) were due to the frequent burning activities in the nearby surroundings for warming purposes.

During April and May, at Monora Peak, Srivastava et al. [210] observed morning and evening BC peaks at 08:00 and 17:00 LST respectively, while during January and February a single evening peak was observed at 17:00 LST. Raju et al. [94] reported afternoon peaks from 12:00 – 13:00 LST (1.64 μg/m³) and an evening peak from 21:00 – 23:00 LST (1.31 μg/m³) with a day/night time ratio of 0.86 over Sinhagad (High altitude site in India) during April, May, December and January. Pant et al. [98] reported a late afternoon peak at 17:00 at
Monora Peak during December 2004. Babu et al. [54] reported that during May in Hanle (India), a morning peak appeared at 08:00 LST and another in the evening at 23:00 LST; also, in June, they observed a morning and evening peak at 07:00 and 23:00 LST, respectively.

The diurnal variation in BC was more prominent in November and December as compared to May and June for all study sites. In winter months, the great diurnal concentration of BC was due to burning of coal, open burning of woods for the generation of heat and wood fire for residential cooking [211].

The change in the anthropogenic emissions, surface meteorology and corresponding boundary layer height affects the diurnal variation in BC concentrations [212]. The peaks during morning time might be due to increased anthropogenic activities and mixing of the nocturnal residual layer aloft with the surface layer after sunrise owing to warming and lifting of the boundary layer cap [100, 213]. During daytime the increased solar heating enhances turbulent effects and a deepening of the boundary layer, which dilutes BC levels. The evening peaks are due to a shallower boundary layer concentrating pollutants such as BC. When night progress, the BC concentration also decreases owing to reduced anthropogenic activities in night hours. According to Stull [213], the BC increase from the mid-afternoon and peak at ~23:00 LST, which is associated with the thinner boundary level and low WS at nighttime.

At different places in India, the same types of daily variation in the mass concentration of black carbon aerosol were observed by different researchers [214-216].

6.5 Impacts of Meteorology on BC

The relationship of BC with local meteorological parameters (Temp, WS and RH) over the study locations are shown in the Table 6.1. During all months at all locations, the BC concentrations exhibited positive correlations with temperature and WS, but a negative correlation with RH. The high correlations of BC with temperature and WS were observed during May and June as compared to November and December. The reason for the positive
Correlation between BC and temperature is that tourism attracts large numbers of people and thus increases vehicular traffic, during spring and summer months. During May and June, the increase in temperature causes higher dispersion of pollutants from neighbouring areas towards the measurement sites, which are at higher levels [217].

Similarly, the reason for the positive correlation of BC and WS was that the rise in WS results in mixing and ventilation, thus transporting aerosols to the receptor sites. There are various reasons for the high black carbon aerosols mass concentration during winter but one of the reasons is that the winter season is drier than summer. At a high altitude site of Ooty (India), Udayasoorian et al. [217] also point out a positive relationship of BC with both wind speed and temperature, which is similar to our results. Sarkar et al. [218] also found a positive association of BC and Temp over Darjeeling. Likewise, Bibi et al. [101] found a negative relationship of BC and RH (R = -0.83) over Karachi (Pakistan). Cao et al. [25] and Tiwari et al. [26] also noted a negative connection of BC with RH.

**Table 6.1:** Correlation coefficient (R) between BC, temperature, wind speed and relative humidity for the four study sites.

<table>
<thead>
<tr>
<th>Variable</th>
<th>May</th>
<th>June</th>
<th>November</th>
<th>December</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Astore</td>
<td>Gilgit</td>
<td>Sost</td>
<td>Skardu</td>
</tr>
<tr>
<td>Temp</td>
<td>0.8</td>
<td>0.7</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS</td>
<td>0.9</td>
<td>0.7</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RH</td>
<td>-0.3</td>
<td>-0.4</td>
<td>-0.6</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.8</td>
<td>-0.7</td>
<td>-0.9</td>
<td></td>
</tr>
</tbody>
</table>

### 6.6 Long Range Transportation of Black Carbon Aerosols

For specific days the HYSPLIT model [122] investigated the origin of air masses arrived the receptor sites at three altitudes e.g. 500, 1000 and 1500 m amsl. Figure (6.6) revealed five-day back trajectories arriving at Astore, Gilgit, Sost and Skardu. At Astore, Gilgit, Sost and
Skardu during May and June, the most common sources of air masses were from Kazakhstan, Uzbekistan, Turkmenistan, Kyrgyzstan, Azerbaijan, Afghanistan and China. In addition to these sources, the air masses also reached to (i) Astore from Iran, Iraq, Georgia and India (ii) Sost from Iran, Iraq and Garjia (iii) Skardu from India and Nepal. Similarly, during November and December the air masses reached to the receptor sites from Kazakhstan, Uzbekistan, Turkmenistan, Kyrgyzstan, Azerbaijan, Afghanistan, China, Kuwait and the United Arab Emirates. Apart from the above sources, the air masses also reached to (i) Astore from Turkey and Bahrain (ii) Gilgit from Iran, Bahrain, Iraq and Garjia (iii) Sost from Saudi Arabia and India (iv) Skardu from Iran, Turkey, Bahrain, Iraq and Garjia.
Figure 6.6: Five-day backward paths of air masses at elevations of 500, 1000 and 1500 m amsl reaching at receptor locations at (a) Astore (b) Gilgit (c) Sost (d) Skardu.
6.7 Comparison of BC with other High Altitude and Urban Environment

Table 6.2 presents a comparison of observed monthly average values of BC concentration at Astore, Gilgit, Sost and Skardu with those reported at other locations. During May at Astore and Gilgit and during June at Skardu, our reported values of BC concentration are higher than all other high altitude except Dehradun, while at Sost during the above months, the BC values were greater than at Hanle and NCOP Nepal and less than other stations. During November and December, our measured BC values at all locations exceed those of other higher altitude locations except Kullu and Dehradun, as these locations are at low altitudes than our locations. Likewise, the most interesting observation was that the BC concentrations of some of these high altitude stations were comparable or higher than at some of the urban locations, which means that these locations represented an urban environment over HKH regions in Pakistan. The higher BC concentration over these high altitude locations were of great concern and draws a serious attention, because it could cause the increase in the atmospheric heating rate over these high altitude location in the HKH mountain regions of Pakistan. Udayasoorian et al. [217] carried the same type of comparison of BC mass concentration at high altitude locations in Ooty with that of other high altitude and urban locations. Similarly, Sarkar et al. [218] conducted the comparison of BC mass concentration between Darjeeling with other places in India.
Table 6. 2: Monthly variation of BC mass concentration measured at Astore, Gilgit, Sost and Skardu and comparisons with other high altitude and urban locations.

<table>
<thead>
<tr>
<th>Location (m amsl)</th>
<th>May</th>
<th>June</th>
<th>Nov</th>
<th>Dec</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Altitude stations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Astore (3170)</td>
<td>2.6</td>
<td>--</td>
<td>3.3</td>
<td>--</td>
<td>Present study</td>
</tr>
<tr>
<td>Gilgit (1500)</td>
<td>3.5</td>
<td>--</td>
<td>4.1</td>
<td>4.1</td>
<td>Present study</td>
</tr>
<tr>
<td>Sost (2790)</td>
<td>1.2</td>
<td>0.9</td>
<td>--</td>
<td>2.2</td>
<td>Present study</td>
</tr>
<tr>
<td>Skardu (2680)</td>
<td>--</td>
<td>3.0</td>
<td>--</td>
<td>3.9</td>
<td>Present study</td>
</tr>
<tr>
<td>Kulu (1200)</td>
<td>2.6</td>
<td>2.0</td>
<td>4.5</td>
<td>6.0</td>
<td>Nair et al. [202]</td>
</tr>
<tr>
<td>NCOP Nepal (5079)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.09</td>
<td>Nair et al. [202]</td>
</tr>
<tr>
<td>Hanle (4520)</td>
<td>0.1</td>
<td>0.08</td>
<td>0.07</td>
<td>0.04</td>
<td>Nair et al. [202]</td>
</tr>
<tr>
<td>Nainital (1958)</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
<td>1.0</td>
<td>Nair et al. [202]</td>
</tr>
<tr>
<td>Dehradun (700)</td>
<td>3.9</td>
<td>3.2</td>
<td>5.2</td>
<td>6.7</td>
<td>Nair et al. [202]</td>
</tr>
<tr>
<td>Manora Peak (2000)</td>
<td>1.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Srivastava et al. [214]</td>
</tr>
<tr>
<td>Nainital (1958)</td>
<td>1.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Pant et al. [99]</td>
</tr>
<tr>
<td><strong>Cities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Karachi</td>
<td>2.9</td>
<td>3.5</td>
<td>10.5</td>
<td>4.9</td>
<td>Bibi et al. [102]</td>
</tr>
<tr>
<td>Delhib</td>
<td>9.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Srivastava et al. [214]</td>
</tr>
<tr>
<td>Pune</td>
<td>2.0</td>
<td>1.5</td>
<td>7.8</td>
<td>9.5</td>
<td>Safai et al. [97]</td>
</tr>
<tr>
<td>Anantapur</td>
<td>2.0</td>
<td>1.4</td>
<td>2.7</td>
<td>3.3</td>
<td>Kalluri et al. [103]</td>
</tr>
<tr>
<td>Kolkata</td>
<td>--</td>
<td>--</td>
<td>14.3</td>
<td>--</td>
<td>Verma et al. [219]</td>
</tr>
<tr>
<td>Allahabad</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>25.4</td>
<td>Badarinath et al. [223]</td>
</tr>
</tbody>
</table>

AmSL= above mean sea level.
Chapter 7

Investigations of the Optical and Radiative Properties of BC Aerosol Particles over Four Heighted Locations in Himalayas, Karakoram and Hindu Kush Region (Northern Pakistan)

7.1 Surface Reflectance, Ozone and Water Vapor

The daily variations in the atmospheric parameters (surface reflectance, ozone and columnar water vapor) over the study locations are shown in Figure 7.1 (a-d). Surface reflectance is a fundamental factor used for the calculation of ARF [220] and represents the amount of radiations reflected into space and atmosphere. The surface reflectance is a key factor, because it depends on the concentration of aerosol and its absorptive property [221]. At Astore, Gilgit, Sost and Skardu, the values of surface albedo varied from 0.09 – 0.28, 0.10 – 0.22, 0.17 – 0.31 and 0.20 – 0.42 with an average value of 0.17 ± 0.06, 0.16 ± 0.03, 0.25 ± 0.05 and 0.29 ± 0.07, respectively. The surface albedo range from 0.09 (Astore on 17 Nov) to 0.42 (Skardu on 23 Dec) with an average value of 0.21 ± 0.08 over four locations. At each location, the surface albedo was found to be higher during May and June as compared to November and December except Skardu in which surface reflectance was noted to have high value during December as compared to June.

Ozone is also one of the most important atmospheric parameters, which take part in global climate change with maximum uncertainty [222]. Daily columnar ozone ranged from minimum value of 23 ppb at Sost (13 Dec) to maximum value of 55.27 ppb at Skardu (3 June) with an average of 36.86 ± 9.6 ppb. Columnar Ozone has maximum values in May and June as compare to November and December at each location. Similarly, columnar water vapor was found to be ranged from 0.06 cm (23 May) to 0.78 cm (11 May) at Gilgit (average 0.33 ± 0.14). The water vapors were found to have higher values during May and June as compared to November and December. For the estimation of radiative forcing, the required atmospheric parameters have been described by the various scholars [89, 127, 97, 223]. Bibi
et al. [103] reported maximum values of surface reflectance, water vapors and ozone during May and June than November and December over Karachi. Ramachandran and Kedia et al. [127] also reported greater values of columnar water vapor (June – August). They also found the high and low values of ozone during summer and winter season, respectively. Surendran et al. [224] found higher values of columnar water vapors during August (6.5 cm), September (4.5 cm) in the year (2010) and June (4.2 cm), July (6.4 cm) in the year (2011) over Delhi. Similarly, over Delhi they also reported maximum water vapors during summer and minimum in winter season.

**Figure 7.1:** Water vapor, Surface albedo and Ozone at (a) Astore (b) Gilgit (c) Sost (d) Skardu

**7.2 Daily Variations in BC Aerosols**

The BC mass concentration was obtained every 15 min interval and was utilized to obtain daily average BC values at Astore, Gilgit, Sost and Skardu during the months of May, June,
November and December (2016), as shown in Figure 7.2 (a-b). During the entire study duration, the BC mass concentration shows robust daily variations over the four study locations.

At Astore, during May, the BC concentration varies from 2.22 – 2.90 µg/m³ (average values of 2.58 ± 0.25 µg/m³) and in November it ranged from 2.49 – 3.70 µg/m³ (average values of 3.27 ± 0.42 µg/m³). At Gilgit, during May and December, BC ranged from 2.06 – 4.72 µg/m³ (average of 3.48 ± 0.61 µg/m³) and from 3.52 – 4.67 µg/m³ (average of 4.10 ± 0.42 µg/m³), respectively. At Sost during May and December, the BC varies from 0.95 – 1.62 µg/m³ and from 1.50 – 4.24 µg/m³ (average of 1.23 ± 0.24 µg/m³) and (Average of 2.90 ± 1.03 µg/m³), respectively. Similarly at Skardu during June BC ranged from 0.75 – 4.14 µg/m³ (average of 2.63 ± 0.99 µg/m³) and during December it varies from 3.17 – 4.67 µg/m³ (average values of 3.82 ± 0.64 µg/m³). The highest observed BC value of 6.06 µg/m³ at Gilgit on 1 December and lowest value of 0.75 µg/m³ at Skardu on 2 June (average value of 3.09 ± 1.07 µg/m³) over the study locations. At each location, the BC concentration was reported to be higher during November, December as compared to May and June.
Figure 7.2: Daily variations of BC concentration at (a) Astore (b) Gilgit (c) Sost (d) Skardu

Pant et al. [98] noted BC mass concentration (1.3 ± 0.9 µg/m³) during December 2004 at Monora Peak. During May and December, at Sinhagad (An Indian high altitude station), Raju et al. [94] documented BC concentrations of (0.6 ± 0.6 µg/m³) and (0.9 ± 0.2 µg/m³), respectively. Safai et al. [96] also documented high BC concentrations during November and December and low BC values in May and June at the coastal urban city of Pune (India). Bibi et al. [103] also documented maximum BC mass concentration (7.5 µg/m³) during the month of December and a low BC value (2.9 µg/m³) in June during 2007 over Karachi. Dutkiewicz et al. [123] also reported maximum BC concentration (~ 10 µg/m³) during November - February and minimum value (~ 2 µg/m³) during June - September over Karachi during 2006
to 2007. Ramachandran and Kedia [127] reported the high monthly average BC value of 13.8 µg/m³ during December and a low value of 1.6 µg/m³ during June over Ahmadabad (India). Similarly, Kalluri et al. [102] reported the highest BC value (3.4 ± 1.2 µg/m³) in January and the lowest values (1.1 ± 0.2 µg/m³) in July over Anantapur (India).

7.3 Modeled Derived Factors

With OPAC model, the optical parameters like AOD, SSA and AP were obtained at 500 nm wavelengths. Figure 7.3 (a-d) represents the daily variations in AOD at four high altitude locations. At Astore, Gilgit, Sost and Skardu, the AOD ranged from 0.2 – 0.22, 0.21 – 0.25, 0.20 – 0.23 and 0.20 – 0.24 with an average value of 0.22 ± 0.005, 0.23 ± 0.007, 0.21 ± 0.012 and 0.22 ± 0.010, respectively. The AOD ranged from minimum value of 0.16 at Skardu (2 June) to maximum value of 0.25 at Gilgit (1 December) with an average of 0.22 ± 0.013. At each location, the AOD is high during November, December than May and June.

The daily variations in AP and SSA at study locations are shown in Figure 7.4 (a-d). At Astore, Gilgit, Sost and Skardu the SSA varied from 0.84 – 0.89, 0.78 – 0.90, 0.83 – 0.94 and 0.8 – 0.95 with an average value of 0.87 ± 0.016, 0.83 ± 0.022, 0.89 ± 0.04 and 0.86 ± 0.04, respectively. The SSA values range from minimum value of 0.78 at Gilgit on 1st December to maximum value of 0.95 at Skardu on 2nd June. AP indicates the angular spreading of radiations dispersed by aerosols and is important parameters that control the assessment of aerosol radiative effects. AP is sensitive to the aerosol’s composition and size, just like SSA [225]. At Astore, Gilgit, Skardu and Sost, AP ranged from 0.69 – 0.70, 0.68 – 0.70, 0.69 – 0.70 and 0.69 – 0.70 with average values of 0.70 ± 0.002, 0.69 ± 0.003, 0.70 ± 0.005 and 0.70 ± 0.005, respectively. The AP ranged from minimum value of 0.68 at Gilgit (1st December) to maximum value of 0.71 at Skardu (2nd June).
Das and Jayaraman et al. [226] found the AOD of 0.35, 0.31 and 0.28 over three locations e.g. Ahmedabad, Udaipur and Mt. Abu, respectively. Over Ahmadabad, Ramachandran and Kedia. [127] reported the SSA values derived from OPAC model, varied from 0.64 (December) − 0.95 (June) at 550 nm. Chung and Seinfeld [227] documented that SSA decreases with the increase of BC concentration, indicating the absorption of radiations by BC aerosols. Pant et al. [98] reported that, the SSA value ranged from 0.87 to 0.94 over Monora Peak. At Delhi, Singh et al. [124] documented the SSA values of 0.74 during January and 0.89 during August with an average value of 0.79. The minimum value of SSA indicates the existence of BC aerosol particles. Sing et al. [126] reported that over Delhi, AP range
from minimum values of 0.65 during January to maximum value of 0.74 during June (average of 0.68).

Figure 7.4: Daily variation in SSA and AP over four high altitude stations

7.4 Black Carbon Radiative Forcing (TOA and SRF)

The daily variations in BC ARF (TOA and SRF) over the study locations are shown in Figure 7.5 (a-d). Positive values of radiative forcing shows a net warming effects and negative value indicates a net cooling effects [228]. At Astore during May, at TOA and SRF, the BC radiative forcing, ranged from 2.21 – 9.21 W/m² and -20.12 – -24.31 W/m² with the corresponding average values of 7.13 ± 2.22 W/m² and -22.17 ± 1.31 W/m², respectively. During November, at TOA and SRF, the BC radiative forcing values varies from -5.55 to -9.11 W/m² and -40.53 to -33.55 W/m² with an average values of -8.17 ± 1.20 W/m² and -
38.36 ± 2.75 W/m², respectively. At Gilgit, during May, at the TOA and SRF, the BC radiative forcing ranged from -83.0 to 8.18 W/m² and from -23.75 to -38.18 W/m² with average values of 4.22 ± 2.78 W/m² and -30.71 ± 3.52 W/m², respectively. During November at Gilgit, it ranged from -3.99 to -6.13 W/m² and from -36.29 to -45.49 W/m² with average values of -4.87 ± 0.87 W/m² and -40.59 ± 3.70 W/m², at TOA and SRF, respectively. Similarly at Gilgit during December, it varies from -5.49 to -9.80 W/m² and from -36.95 to -54.41 W/m² with average values of -8.00 ± 1.52 W/m² and -43.71 ± 6.08 W/m², respectively. At Sost during May, at the TOA and SRF, the BC radiative forcing values varies from 5.01 to 8.67 W/m² and from -9.22 to -15.32 W/m² with average values of 6.54 ± 1.42 W/m² and -12.46 ± 2.02 W/m², respectively. During December, it ranged from -0.07 to -9.23 W/m² and from -42.50 to -49.60 W/m² with an average values of -4.53 ± 2.91 W/m² and -32.36 ± 8.81 W/m², at TOA and SRF, respectively. Likewise, at Skardu during June, its values at the TOA ranged from 1.29 to 13.92 W/m² with an average value of 7.88 ± 3.88 W/m² and at SRF it varies from -16.82 to -26.32 W/m² with an average value of -20.70 ± 6.21 W/m². At Skardu during December, at the TOA, the BC radiative forcing varies from -0.23 to 13.89 W/m² with an average value of 5.47 ± 4.89 W/m² and at SRF, the BC values ranged from -26.72 to -40.34 W/m² with an average value of 31.97 ± 4.30 W/m².
Figure 7.5: At TOA and SRF, radiative forcing due to BC aerosols at (a) Astore (b) Gilgit (c) Sost (d) Skardu

7.5 Radiative Forcing with in ATM and Heating Rate

The daily variations in SW BC radiative forcing with in ATM and their resultant Heating Rate (HR) are given in the Figure 7.6 (a - d). At Astore during May and November the BC forcing ranged from 25.72 to 32.17 W/m² (AVG 29.29 ± 2.33 W/m²) and 24.43 to 32.41 W/m² (AVG 30.19 ± 2.96 W/m²) with corresponding HR of 0.82 K/day and 0.85 K/day, respectively. At Gilgit, the BC forcing varies from 22.91 to 44.18 W/m² (AVG 34.93 ± 5.02), 30.90 to 41.49 W/m² (AVG 35.71 ± 4.11) and 27.14 to 48.92 W/m² (AVG 35.70 ± 7.6) with corresponding HR of 0.98, 0.99 and 0.99 K/day, during May, November and December, respectively. At Sost during May and December, its values vary from 14.23 to 23.99 W/m².
(AVG 18.99 ± 3.40 W/m²) and from 15.20 to 44.33 W/m² (AVG 27.82 ± 9.84 W/m²) with corresponding HR of 0.53 K/day and 0.78 K/day, respectively. Similarly, at Skardu during June, the radiative forcing varies from minimum value of 10.14 W/m² to maximum value of 38.89 W/m² (AVG 28.58 ± 9.15 W/m²) with HR 0.80 K/day and during December the values range from 31.64 to 43.85 W/m² (AVG 37.43 ± 4.88 W/m²) with HR of 1.05 K/day.

Figure 7.6: BC radiative forcing and HR at (a) Astore (b) Gilgit (c) Sost (d) Skardu

Generally SW BC, radiative forcing with in atmosphere was observed to have positive values, while at SRF, the negative values of ARF were found. At TOA both negative and positive values were found. Moreover, BC radiative forcing was noted to be maximum during November and December months as compared to May and June. In November and December, the maximum ARF is because of the high concentration of BC aerosols, higher BC AOD, lower SSA, although the surface albedo was found to be low. During May and
June, its value is lower, because of lower BC concentration, low AOD, higher SSA, in spite of the higher values of surface albedo.

Over Indian locations (Ahmadabad, Udaipur and Mt. Abu), Das and Jayaraman, [226] investigated, the BC radiative forcing at the TOA of 1.7, -1.5 and -1.5 W/m², at SRF of -46, -35 and -31 W/m² and atmosphere radiative forcing of 47.7, 35.5 and 29.5 W/m², respectively. The resultant heating rates over the above locations were 1.3, 1.0 and 0.4 °K/day, respectively. Over central Himalaya, Kumar et al. [53] investigated, the radiative forcing (+21 W/m², +40 W/m²) and their corresponding heating rates (0.9 °K/day, 1.7 °K/day) during (low fire and fire-impacted activity), respectively. Latha and Badarinath [97] carried out study over eastern India and reported that at TOA, BC radiative forcing ranged from 0 to 16 W/m² and at SRF, it varied from 0 to -33 W/m². Surendran et al. [224] found the maximum, radiative forcing with in ATM to be 66 W/m² and 65 W/m² during November and December, respectively and minimum of 23 W/m² during July over Delhi. Over Ballia, Tiwari et al. [80] noted atmospheric radiative forcing along with HR for three months i.e. June (42.2 W/m², 1.19 °K/day), July (35.4 W/m², 0.99 °K/day) and August (43.3 W/m², 0.96° K/day).
Chapter 8

Temporal Variations in Aerosol Optical Properties over Dir Upper, a Rural Environment of Northern Pakistan

8.1 Meteorological Condition of the Region

Meteorological data was provided by the Pakistan Meteorological Department Peshawar. The meteorological situation of Dir (Upper) is summarized in Figure 8.1. Maximum and minimum temperature values were observed in month of July (25.42 °C) and January (5.99 °C). Maximum Rain Fall (RF) and Relative Humidity (RH) values were found in February (201.12 mm) and August (55.77 %), but minimum values were observed in the month of June (61.03 mm) and May (41.77 %). Likewise highest Wind Speed (WS) was found in July (1.49 m/s) and the lowest value of WS was observed during January (1.0 m/s).

![Figure 8.1: Meteorological conditions of the area from 2004-2016](image-url)
8.2 Aerosol Optical Depth and Angstrom Exponent

The fundamental parameters, which can estimate the aerosol properties at any locations, are AOD and Angstrom exponent (AE). From the Angstrom power law, AE can be estimated [229].

\[ T_\alpha(\lambda) = \beta \lambda^{-\alpha} \]  \hspace{1cm} 8.1

Where \( \lambda \) denote wavelength, measured in micrometer, \( T_\alpha \) represents the AOD, \( \alpha \) indicates AE and \( \beta \) represents turbidity coefficient. AE greater than 1 shows fine particles whereas AE less than 1 indicates the domination of coarse particle [35, 78].

8.3 Monthly Variation in AOD and AE

Figure 8.2 (a, b) shows the long-term (2004 - 2016) monthly differences in AOD (550 nm) and AE (470 - 870 nm). There is a large variation in both AOD and AE, suggesting the variations in aerosols types [230]. Minimum value of AOD was found in December whose values vary between 0.04 and 0.16 (Average 0.09 ± 0.04). Similarly, a maximum value of AOD was found in the month of July and varies from 0.23 to 0.42 with average values of 0.30 ± 0.05. The minimum and maximum values of AE was observed in May and December whose values range from 0.41 to 0.64 and 1.00 to 1.32 with an average value of 0.51 ± 0.07 and 1.17 ± 0.09, respectively. The variation in AOD and AE is due to the various emission sources as well as their emission rates, long range transport of atmospheric aerosols, different atmospheric condition and boundary layer dynamics [84]. Figure 8.2 (a, b) represents a converse relation of AOD with AE. Such type of inverse relation between the two parameters i.e. AOD and AE was early described by Tiwari et al. [80]
Figure 8.2: Box-whisker plots summarizing monthly variations in (a) AOD (b) AE over the entire study region.

8.4 Seasonal Variation in AOD and AE

Figure 8.3 (a, b) reported the seasonal wise difference in AOD (550 nm) and AE (470 – 870 nm) from 2004 to 2016. The AOD varied from 0.17 – 0.28, 0.21 – 0.38, 0.13 – 0.25 and 0.04 – 0.21 with an average value of 0.22 ± 0.04, 0.28 ± 0.05, 0.17 ± 0.04 and 0.12 ± 0.05 during four seasons e.g. spring, summer, autumn and winter, respectively. Similarly, the values of AE during the above four seasons ranged from 0.45 – 0.63, 0.52 – 0.79, 0.81 – 1.10 and 0.93 – 1.13 with an average value of 0.56 ± 0.04, 0.62 ± 0.07, 0.96 ± 0.08 and 1.030 ± 0.07, respectively. Various emission sources of aerosols, atmospheric circumstances, boundary layer dynamics and transportations of aerosols from long range are responsible for the variations in AOD and AE [231]. Lower values of AE were found from March to July indicating the transportations of aerosols (dust) from Middle East and Thar Desert into the region [232]. The AE values greater than 1 are found during November, December and January, suggesting the presence of fine mode particles. The AE greater than 1 in autumn and winter was noted by Srivastava et al. [210] over Indo-Gangetic Plane (IGP) indicating the domination of fine aerosol. Previous research study also indicated the fine aerosol during the two seasons (autumn and winter) over IGP [233- 235].
Figure 8.3: Box-whisker plots representing seasonal variations in (a) AOD (b) AE over the study region.

8.5 HYSPLIT Trajectories

In ordered to find out the air masses reaching to the study location, seven days back trajectories bringing aerosols ending at height (500 m) above the sea level were investigated by means of HYSPLIT model (Figure 8.4). These trajectories are calculated at different months of the study period, representing four seasons. During spring, summer and autumn long range trajectories were observed, which bring coarse mode aerosol particles to the study region. During winter, trajectories were generated locally indicating fine mode aerosol particles.
Figure 8.4: Seven-day back trajectories indicating the air mass at height of 500 m reaching Dir (Upper) on a specific months of April 2006, July 2009, November 2009, December 2006 representing four seasons.
Chapter 9

Conclusions and Future Work

9.1 Conclusions

In this research work, the physical, chemical and optical characteristics of aerosols were studied over various study locations.

Due to increased urbanization, industrialization, transportation and constructions of roads, buildings and overhead bridges in Peshawar (Pakistan), PM have increased significantly and are in excess of WHO limits. The aerosols emitted from regional sources have significantly harmed the air quality of the city. In Peshawar city, the 24 hours average concentrations of PM$_{2.5}$ was 286 µg/m$^3$ and of PM$_{10}$ was 638 µg/m$^3$, which was 11 (PM$_{2.5}$) and 13 (PM$_{2.5}$) times higher than the recommended WHO limits. Morphological analysis of PM revealed that the following groups of particles were present in Peshawar: geogenic, anthropogenic and biogenic. In geogenic particles, aluminosilicates were the main contributor. Among anthropogenic aerosols, carbonaceous particles were the most abundant due to extensive fuel combustion and biomass burning. Biological particles were very few in number. Aerosols emitted from vehicular exhaust were the main contributor to the particulate matter, resulting the poor air quality in the city. The remaining aerosols were mainly generated from road dust and fossil fuel combustion. Bonds between different components were determined by FTIR Spectroscopy.

In the present study, remote sensing data are analysed to examine seasonal and monthly variations in aerosol optical properties, as well as ARF between 2004 and 2016 over northern Pakistan. For the whole area, maximum values of AOD (0.60 ± 0.06) and SSA (0.97 ± 0.006) were observed in spring, while the maximum values of AI and AAOD occurred in winter (0.78 ± 0.20) and summer (0.020 ± 0.002). Minimum values of AOD, AAOD and SSA occurred in winter (0.28 ± 0.03, 0.009 ± 0.004 and 0.969 ± 0.011), while the minimum value
(0.68 ± 0.09) of AI was observed in autumn. Trend analysis reveals that AI, AOD and AAOD exhibited an increasing trend, while SSA shows decreasing trend. The maximum value of radiative forcing within ATM was observed in summer (54.34 ± 7.31 W m⁻²) and minimum values occurred during winter (31.51 ± 6.23 W m⁻²). The CALIPSO measurement revealed that various aerosol types impacted the study region. The analysis of the HYSPLIT cluster trajectories revealed that, air masses reaching the studied receptor sites were, from Iran, India, Afghanistan, Turkmenistan, Tajikistan, Azerbaijan, Sialkot, Peshawar, Cholistan Desert and from local regions. From all analysis, it was concluded that, the leading absorbing aerosol particles were dust during spring and summer seasons, while pronounced absorbing aerosols were mixed anthropogenic during autumn and winter seasons. Moreover, the results derived from the OMI were confirmed by CALIPSO measurements and HYSPLIT trajectories.

The mass concentration of BC aerosols were continuously monitored over four locations in northern Pakistan (Astore, Gilgit, Sost, Skardu) during May, June, November and December of 2016. The highest average BC mass concentration of 4.1 ± 0.4 µg/m³ was observed at Gilgit during November and at Skardu during December, while the lowest BC (0.9 µg/m³) was observed in Sost during June. The BC concentrations were higher during November and December as compared to May and June at all locations. BC aerosols show diurnal variations with two peaks (morning and evening) linked with regional anthropogenic and migrated aerosols. BC concentrations were sharply enhanced in morning time from 8:00 to 12:00 LST, followed by a slowly decreasing trend with low values around 17:00 LST, and then increasing during the evening time from 20:00 – 23:00 LST. The HYSPLIT model revealed the migrated aerosol from multiple locations (e.g., Turkmenistan, Uzbekistan, Kazakhstan, Kyrgyzstan, Azerbaijan, Afghanistan, Turkey, Iran, Iraq, Kuwait, United Arab Emirates, Turkey, Bahrain, Saudi Arabia, China, and India) to the studied sites. BC
concentrations exhibited positive correlations with temperature and wind speed and negative with RH.

The study of the daily variations in the aerosols optical properties, obtained from OPAC models utilizing surface based measurement of black carbon at four high altitude stations (northern Pakistan) and their climatic impacts has been conducted during May, June, November and December (2016). BC mass concentration varies from 0.75µg/m³ at Skardu on 2-June to 6.06 µg/m³ at Gilgit on 1-December 2016. BC is found to have maximum values during November, December than May and June. BC AOD ranged from minimum value of 0.19 on 2-June at Skardu to maximum value of 0.25 on 1-December at Gilgit. SSA and AP ranged from 0.78 (1-December) to 0.95 (2-June) and 0.68 (1-December) to 0.71 (2-June) with an average value of 0.86 ± 0.04 and 0.70 ± 0.008. The BC radiative forcing at Astore, Gilgit, Sost and Skardu at TOA, SRF were -0.009 and -29.71, -0.81 and -36.12, 0.026 and -24.17, 6.9 and -25.08, respectively. The BC radiative forcing within ATM at Astore, Gilgit, Sost and Skardu were 29.71, 35.31, 24.19 and 32.02 W/m², respectively. Similarly, their resultant HR over these locations was 0.83, 0.99, 0.68 and 0.90 K/day, respectively.

To know the microphysics and variability of aerosol at Dir (Upper), the continuous measurement of AOD and AE was performed for long period (2004–2016). Maximum and minimum monthly values of AOD were found in July (0.30 ± 0.05) and December (0.09 ± 0.04), respectively. Maximum AE was observed in December (1.17 ± 0.09), while minimum AE was reported in May (0.51 ± 0.07). Similarly, seasonal AOD during spring, summer, autumn and winter were noted to be 0.22 ± 0.04, 0.28 ± 0.05, 0.17 ± 0.04 and 0.12 ± 0.05, respectively. The AE values of 0.56 ± 0.04, 0.62 ± 0.07, 0.96 ± 0.08 and 1.030 ± 0.07 were observed during the four seasons, respectively. The HYSPLIT model showed that different particles were transported during different seasons.
9.2 Future Work

The research work presented in this thesis explains the current knowledge of the aerosol physical, chemical and optical properties and their climatic implications. In the Present work the chemical and physical properties of PM have carried out over urban environment of Peshawar by using techniques like SEM-EDX and FTIR. This work can be extended over different environments by using other experimental techniques like Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Transmission Electron Microscopy (TEM), Proton Induce X-ray Emission (PIXE).

The optical properties of aerosols over the glacier region (Astore, Gilgit Skardu) has been investigated from 2004-2016. This work can be extended over various environments across the world for other observation period to better understand the reliability of satellite sensors.

In the present work BC aerosol properties and their radiative properties has been explain over glacier region. As the transportation of BC aerosol is common process and its concentration mainly depends on source region, therefore, further investigation of BC in other region are needed in future. Furthermore, the optical properties of BC aerosols can also be simulated by using other models in ordered to improve the accuracy of the data. This work is about the direct effect of absorbing aerosol and indirect effect is not included, therefore, we can explore this avenue of research in future. The reduction in the surface reflectance over the glacier due to BC aerosols can be further studies in detail.
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