Chapter 1

Introduction

Earth's atmosphere is predominantly a nitrogen-oxygen atmosphere, these two gases occupying about 99% by volume. A whole host of minor and trace constituents contribute to the remaining 1% which include argon, carbon dioxide, water vapour, ozone, methane, oxides of nitrogen, carbon monoxide, hydrogen sulphide, ammonia etc. which occur in minute quantities - parts per million to parts per trillion by volume and more importantly aerosols vie with each other in playing a vital role in determining the conditions on the Earth's surface and in the biosphere. In spite of their small proportion by volume the mankind is concerned about these minor constituents because of their distinctive but very important roles in the physico-chemical and related activities in the atmosphere. The sources and sinks of atmospheric particulate matter (*aerosols*), their physical and chemical properties and their residence times are of special interest, primarily because their size and composition can be readily noticed than gaseous pollutants and they are a link in the chain of the removal process which returns gaseous pollutants to the Earth's surface.

1.1 Atmospheric aerosols: Classification, production and removal processes and effects

Atmospheric aerosols are a mixture of solid or liquid particles suspended in the medium of air. Their physical (size, shape and texture) and chemical properties vary over a wide range and consequently their removal processes and hence their residence times vary greatly. Aerosol particles of different sizes and composition play a vital role in many atmospheric processes such as visibility, radiation balance, atmospheric electricity, air pollution, cloud formation etc. The sizes of aerosols extend over several orders of magnitude from 0.001 μm to 100 μm, sweeping from a cluster of molecules at one end to hailstones at the other end. They are in general divided into three categories based on their sizes:

(i) Aitken nuclei (0.001 μm $< r <$ 0.1 μm)
(ii) Large particles (0.1 μm $< r <$ 1.0 μm)
(iii) Giant particles ($r >$ 1.0 μm)

Particles in the size range below 1.0 μm are formed mostly through gas-to-particle conversion process, while particles larger than 1.0 μm are formed directly by mechanical processes such as wind blown dust, sea salt droplets produced by breaking bubbles on the sea surface, pollen grains etc. The fine particles size mode (which incorporates both Aitken nuclei and large particles) is made up of two distinct populations. The particles at the lower end of the size spectrum (Aitken nuclei or transient nuclei) have a short residence time in the atmosphere as they are chemically active and also due to their physical mobility. These particles will eventually get transformed into 0.1 - 1.0 μm size particles, generally referred to as accumulation mode, through processes such as nucleation, condensational growth and coagulation. The coarse mode accommodates particles larger than 1.0 μm. The production source of aerosols determines the chemical composition while the formation mechanisms determine the size spectrum and shape of the particles. Chemical composition, size range and shape decide the ability of a particle to interact with electromagnetic radiation. The source strength of any particle determines by and large the importance of a component by virtue of its mass concentration and number density. The sources of aerosols can be classified into *primary* and *secondary.* The primary or direct sources which are mostly of natural origin include, the world oceans (covering two thirds of the Earth's surface, sea salt particles), arid and semiarid regions (wind blown soil dust), terrestrial biota (biological material of plant origin), smoke from burning of land biota and direct anthropogenic particle emissions, for example soot, smoke, road dust etc., terrestrial ejecta (volcanic effluvia, which includes direct particle emissions and products derived subsequently from reactions of emitted gases) and meteorites (extraterrestrial and interplanetary dust). The secondary or indirect source, which is the major source of particles below 1 μm in radius, is the conversion of the available natural and man-made atmospheric trace gases into solid and liquid particles. This process called as *gas-to-particle conversion mechanism* depends on a number of precursors which include sulphur and nitrogen bearing gases among others.

While due to above processes aerosols are incessantly created and transformed, the existing ones are also regularly removed from the atmosphere by a wide variety of dry and wet removal processes. Dry deposition include settling of particles by gravitation and impaction and diffusion of particles to surfaces and wet removal is by rainwash. The removal efficiencies are a function of the particle size. Hence when a specific aerosol is subjected to a large number of conversion and removal mechanisms which are size dependent, the overall residence time of that particle will be governed by the competing effects of all the conversion and removal processes acting on the particle. For particles in the size range of 0.01 to 10 μm the residence time in the lower troposphere is about a week, while in the upper troposphere they reside up to a few months. In stratosphere the residence time extends to few years. The variation in the residence times of aerosols with respect to altitude stems from a variety of factors, principal being the distribution of water vapour which affects conversion and removal processes and the vertical distribution of a number of reactant gases which include SO_2, COS, CS_2 etc. The aerosol number density shows variations with altitude and as well with seasons in the troposphere. For example, over the Indian subcontinent, the aerosol number density in the lower troposphere is about a few thousands of particles during the pre-monsoon period, while after the monsoon their number is reduced to a few hundreds, due to rainwash. In the stratosphere, in volcanically quiescent i.e. background conditions the aerosol number density is about a few particles, while after major volcanic eruptions the number can go up by more than one order of magnitude. Most of the aerosols are concentrated between 0 and 35 km in the atmosphere, while the bulk of them are in the troposphere which vary with seasons and locations and subsequently produce regional effects, the stratospheric aerosols are longlived and can produce global effects.

The atmospheric aerosol plays a vital role, in many processes which impact our lives either directly (health) or indirectly (climate), the most obvious manifestation being haze. Scattering and absorption of solar radiation and the formation of clouds and fog by cloud condensation nuclei are of more fundamental importance. The aerosol particles by capturing the small ions influence the electrical conductivity of air.

The size distribution of stratospheric aerosols generally is a unimodal distribution as they are formed mainly due to gas-to-particle conversion mechanism, while the tropospheric aerosols are made up of two to three modes depending on their production environments i.e. whether urban, continental, maritime, desert etc. and are further influenced by meteorological phenomena. Thus as the properties of tropospheric aerosols are much more variable on time and space scales because of the great diversity and wide distribution of sources and their short residence times, in many ways it is more difficult to study tropospheric aerosols than stratospheric aerosols, which have a residence time of about a few years.

1.2 Need for aerosol studies

The study on aerosols can be broadly classified into two leagues, though they are interrelated.

(i) As a group of atmospheric constituents that can be defined chemically and physically, aerosols themselves. Basic questions of characteristics of aerosols, their composition, their residence times, their major sources and sinks and their size distributions fall under this category. Just as in any other field of science, basic information about aerosols is warranted.

(ii) The other genre of study involves the associated processes of aerosols and their effects in the radiative transfer and climate.

Some key issues regarding aerosols and their effects about which the scientific community is apprehensive are as follows:

Recent study of *Charlson et al.* [1992] suggests that tropospheric aerosol, contributes substantially to radiative forcing and anthropogenic sulphate aerosol in particular has imposed a major perturbation to this forcing. This perturbation is comparable in magnitude to the current anthropogenic greenhouse gas forcing but opposite in sign. So it is essential to take aerosol effects into account while evaluating anthropogenic influences on past, current and future climate. As a number of aerosol related phenomena depend nonlinearly on aerosol concentrations, the influence of the anthropogenic aerosols depends nonlinearly on their emissions and their interactions with the natural background aerosol. Also as aerosols are shortlived in atmosphere unlike the principal greenhouse gases and as the aerosol forcing is greatest in daytime and in summer, whereas greenhouse forcing acts over the full diurnal and seasonal cycles, the anthropogenic aerosols perturb radiative forcing differently than greenhouse gases in many important ways. Some of the key questions which remain unanswered regarding the climatic influence of anthropogenic aerosol and its relation to the increased concentrations of greenhouse gases are, how these forcings compensate each other physically, altitudinally, geographically and temporally and to what degree, among others. In addition to the tropospheric aerosols, as the concentration of sulphate aerosol in the lower stratosphere is also increasing due to aircraft emissions [*Hofmann,* 1990], sporadic volcanic eruptions etc., which inject lot of SO_2 into the stratosphere, stratospheric changes must also be taken into account while considering climate trends.

Recent model calculations by *Alkezweeny* [1995] on the anthropogenic sulphur dioxide emissions and sulphate concentrations indicate that the cooling effect of sulphate aerosols overwhelms the greenhouse warming. He also suggests that the increase in the sulphate aerosols of the past one hundred years may have caused a global cooling of about 2°C and he recommends more measurements of sulphate mass concentrations and cloud condensation nuclei to prove this trend. *Kaufman et al.* [1991] reached a similar conclusion from the analysis of fossil fuel and biomass burning impact on the global climatic change. Alkezweeny also established a nonlinear relationship between the sulphate concentration and sulphur emission and this nonlinearity was explained in terms of the difference in the tropospheric residence times of sulphur gases and aerosols. While SO_2 stays up to one to three days in the atmosphere, the aerosols in the size range of 0.1 - 1 μm in diameter can stay a week in the troposphere. It's important to mention that nearly all sulphate aerosols are in this size range [*Whitby,* 1978]. In the recent past during the post-industrial era, as the number of power plants and industry is on the rise and due to fossil fuel and biomass burning escalation, anthropogenic aerosols have increased near the source regions and majority of these aerosols are sulphate aerosols. A detailed analysis of temperature and aerosol emission records for large areas of the northern hemisphere indicates a persuasive evidence of aerosol cooling [*Kerr,* 1995] and the aerosol cooling effect is found to be strongest where aerosol pollution is heaviest and it changes with time depending on emissions. These results show that now there is a substantial evidence which points out a cooling effect due to aerosols and to assess and understand the regional and global climate changes, aerosols are an essential ingredient. In the light of these results now it has become clear that sulphate aerosols from volcanic eruptions and fossil fuel combustion exert a cooling influence on the climate. While this effect is an established one, estimates of magnitude, trends and extent of cooling effects are uncertain. This uncertainty mainly arises from limitations in the observations of aerosol amount and composition both in the troposphere and stratosphere globally, limitations in the models used to simulate the aerosol system and the indirect influence of sulphate aerosols in cloud extent and character.

Atmospheric aerosols affect indirectly the cloud microphysical characteristics. Cloud droplets are formed in the lower atmosphere by condensation of water on existing aerosol particles. Sulphate aerosols, being water soluble, act as good condensation nuclei and seem to dominate the anthropogenic influence on cloud condensation nuclei. They take part in the cloud formation and wield an influence on the cloud droplet size distributions. By affecting the amount, type and distribution of clouds, aerosols could alter the radiation balance of the Earth.

Volcanic aerosols can cause warmings (of about 3-4°C) in the stratosphere primarily due to the absorption of upwelling terrestrial radiation and by reducing the amount of total solar radiation reaching the troposphere, can cause cooling (of about 0.5°C) globally [*Ackerman,* 1988] and also these aerosols by backscattering (as these aerosols are efficient scatterers but only weak absorbers at visible wavelengths) more amount of solar radiation into space, increase the planetary albedo. Major development during the recent years has been the finding of active participation of volcanic aerosols in heterogeneous chemistry, which accelerates stratospheric ozone depletion. Also the transport caused by heating of the aerosols and the resultant lofting of the stratospheric airmass has been identified as one of the key players in ozone depletion, in the post-volcanic period [*Grant et al.,* 1994]. Significantly the order of importance of these two phenomena is not yet ascertained. Though it was found initially that the processes which are responsible for ozone depletion in mid and higher latitudes [*Hofmann and Solomon,* 1989] are not active in the tropics, recent observations on ozone depletion in the tropics by *Grant et al.* [1992, 1994] and *Hofmann et al.* [1994] have proved the other way. The continued decrease of stratospheric ozone till mid-1992 (an year after Pinatubo eruption) raises a question whether the ozone loss mechanisms are continuing to operate or whether the ozone recovery mechanisms are not as rapid as had been estimated [*Grant et al.,* 1994], as tropics is the source region for ozone.

These issues can be addressed if a reliable data base exists, so that more realistic aerosol parameters can be used instead of scalable parameters while modeling as well as to assess the impact of these aerosols.

1.3 Importance of tropical aerosols

It has been shown that the tropical lower stratosphere and tropical tropopause are more sensitive to perturbation in radiative heating rates than at other latitudes [*Ramaswamy,* 1988a]. Further, arid and semiarid regions of the world, which are the major sources for the wind blown mineral particles and most of these regions lie along the tropical belt, making it important to study about these particles as well their transport inland. The optical properties of these particles can help in the assessment of their impact on the radiation balance and hence on climate.

Volcanic eruptions, though are a disaster for those living nearby, provide an exceptional opportunity for atmospheric scientists to understand the various processes involved in the formation of stratospheric aerosol layer, its decay and the climate effects and hence should be studied in greater detail as a valuable experiment on the nature and should be exploited as a natural resource to enhance our knowledge of the working of this complex atmosphere and climate system. Documentation of the scientific data and assessment of the impacts form the first crucial step in the process of evaluating the radiative, dynamical, chemical and climatic effects due to volcanic aerosols, to provide us with a glimpse into the future. As most of the active volcanoes lie along the tropical belt and also as the ejecta from an equatorial volcano can have a wider global coverage, the tropical stratosphere becomes a very vital region to study the optical and physical properties of volcanic aerosols.

1.4 Indian scene

Observations of solar radiation and atmospheric turbidity started in late 1950s in India during the International Geophysical Year (1957) using pyrheliometers over Pune and Delhi [*Mani and Chacko,* 1963]. In the 1970s using Sun photometers haze extinction coefficients were obtained for over an year and turbidity coefficients and Ångstrõm wavelength exponent α were determined over Pune [*Rangarajan,* 1972]. Though the measurement of aerosol properties started about 4 decades before in Pune, not until 1980s an immense need was felt to study these properties systematically, on a long term basis over the Indian subcontinent. With this in view Indian Middle Atmosphere Programme was established in 1980s and multiwavelength radiometers to study tropospheric aerosols over various Indian stations were established [*Krishna Murthy,* 1988; *Krishna Moorthy et al.,* 1989] and aerosol number density and size parameter measurements were made using rocket- and balloon-borne Sun photometers [*Subbaraya and Jayaraman,* 1982; *Jayaraman et al.,* 1987] up to stratospheric altitudes. Chemical composition and size distribution of aerosols in the size range of 0.4 to 10.0 μm were studied using an Andersen particle sampler over Pune [*Khemani et al.,* 1982] and other locations over India [*Negi et al.,* 1987; *Khemani,* 1989]. Aerosol characteristics could be determined up to 28 km with a pulsed ruby lidar over Trivandrum [*Parameswaran et al.,* 1991] and a helium-neon lidar was operated over Pune to study aerosol characteristics up to a few hundreds of metres, which then later was extended up to about 5 km using argon ion laser [*Raj and Devara,* 1989; *Devara and Raj,* 1991]. However, for an assessment of the effect of aerosols on the Earth-atmosphere radiation budget, both, columnar aerosol optical depth, a measure of the amount of aerosol in the atmosphere, which is a function of wavelength, airmass, season, altitude, latitude and proximity to source, is vital in studying the tropospheric climate changes relevant to the location of measurement, and vertical profiles of aerosol extinction, size parameter, number density and asymmetry factor are important in studying the radiative effects of stratospheric aerosols, at various altitudes, especially after major volcanic eruptions and these data on various parameters will go a long way in addressing some of the key issues of aerosols.

1.5 Objective and Scope of the present investigation

The objective of this work has been to study the characteristics of tropospheric and stratospheric aerosols in the tropical middle atmosphere. Optical investigations using ground based and balloon-borne photometers and lidar are made and the results are reported herein. The thesis focuses on the optical properties of tropospheric aerosols, their day to day and seasonal variations and of stratospheric aerosols, their formation, evolution and decay, after the Mt. Pinatubo eruption as observed over the tropical locations Hyderabad (17.5°N) and Ahmedabad (23°N).

The scope of the present work can be broadly classified topicwise into tropospheric and stratospheric aerosols.

- Using a newly developed Sun-tracking photometer the temporal variations of tropospheric aerosols over Ahmedabad, from 1991 to 1995, the day to day variations, diurnal variations, spectral dependence of aerosol optical depths, variations in wavelength exponent and the relation of aerosol optical depths to the day's maximum temperature and relative humidity are studied and the results are discussed. The results obtained include the effects of Gulf oil fires of 1991 and Mt. Pinatubo eruption in 1991 on the aerosol optical depths.

- Two high altitude balloon flights were conducted from Hyderabad (17.5°N, 78.6°E) during October 1991 and April 1992 to study *in situ* the optical properties of aerosols at the stratospheric altitudes produced due to the Pinatubo volcanic eruption occurred in

June 1991. Sun-scanning and Sun-tracking photometers were employed to measure the scattered and the direct solar radiation intensities and the results obtained on the vertical profiles of aerosol extinction coefficients, number density, size distribution parameter, mode radius, asymmetry factor and mass of Pinatubo aerosols are presented and discussed.

- Using a newly set up Nd:YAG backscatter lidar system at the Physical Research Laboratory (PRL), Ahmedabad (23°N, 72.5°E) the Pinatubo aerosol layer was studied from April 1992 to May 1994. Results obtained on the vertical profiles of scattering ratios, aerosol extinction coefficients and aerosol mass are discussed and their time evolutions are studied.

- A simple model taking into account the aerosol microphysical processes of growth, coagulation and sedimentation was developed to study the time evolution of a volcanic aerosol layer in the stratosphere. The model results are compared with balloon, lidar and satellite data for Pinatubo as well as with El Chichon data available in literature.