Chapter 1
Chapter 1
Introduction

1.1 Background

Aerosols are defined as solid or liquid particles suspended in the atmosphere. Dust, smoke, mist, haze, fog, soot and smog are various forms of common aerosols. This terminology of particular aerosol is described depending on the characteristics, size and shape. Aerosols play an important role in every aspect of the atmospheric processes such as meteorology, radiation balance, atmospheric chemistry, air pollution and human health. Aerosols are minute particles suspended in the atmosphere. When these particles are sufficiently large, we notice their presence as they scatter and absorb sunlight. Aerosols interact both directly and indirectly with the Earth's radiation budget and climate. As a direct effect, the aerosols scatter sunlight directly back into space. As an indirect effect, aerosols in the lower atmosphere can modify the size of cloud particles, changing how the clouds reflect and absorb sunlight. Aerosols are present throughout the boundary layer, at different number concentrations depending upon factors such as location, atmospheric conditions, annual and diurnal cycles and presence of local sources. The highest concentrations are usually found in urban areas, reaching up to $10^8$ and $10^9$ particles per cc (Seinfeld and Pandis, 1998).

Aerosols play a critical role in the atmospheric composition by governing the rate of reactions between the chemical species. Most of the chemical pollutants e.g. NOx, Ozone, VOCs are photochemically active and the incoming radiation determines the decay of these pollutants, along with formation of secondary pollutants from these precursors. Aerosols also can act as sites to take place chemical reactions (heterogeneous chemistry). The most significant and well known of these reactions are those that lead to the destruction of stratospheric ozone (Farman et. al., 1985). During winter in the Polar Regions, aerosols grow to form polar stratospheric clouds. The large surface areas of
these cloud particles provide sites for chemical reactions to take place. These reactions lead to the formation of large amounts of reactive chlorine and ultimately, to the destruction of ozone in the stratosphere. Evidence now exists that shows similar changes in stratospheric ozone concentrations occur after major volcanic eruptions like Mt. Pinatubo in 1991, where tons of volcanic aerosols are blown into the atmosphere (McPeters, 1993).

These aerosols are generated or pumped in the atmosphere by various ways like wind blown over deserts, sea spray, volcanic dust, forest or man made fires, industrial and vehicular activities and photochemical reactions. The impact of aerosols is a function of size and chemical composition. The composition and size of aerosols are controlled by their sources and the physical and chemical processes, which they undergo in the atmosphere. The size of aerosols spans several orders of magnitude, ranging from several nanometres to hundreds of micrometers (Seinfeld and Pandis, 1998). The lifetime of these aerosols in the atmosphere is from days to weeks in troposphere and from months to years in case of stratosphere. The concentration decreases with the increasing height in the atmosphere. The residence time of a particle in the atmosphere is strongly determined by the size and therewith the mass of a particle.

Human activity influences atmospheric composition on a local and global scale (Houghton et. al. 2001). Primary emissions in the planetary boundary layer and the free troposphere over densely urbanized regions generate plumes of secondary pollutants. The industrialization of modern times associates with different phenomena, not the least of which is an increasing amount of air pollution in the densely populated cities of developed countries (Cooper, 1998). The resulting mixture of primary and secondary pollutants then can be transported over and affect wide area. Anthropogenic pollution combined with some natural atmospheric compounds and particles has a significant impact on human health and the environment.

1.2 Formation of Aerosols

Aerosols are formed by mainly two mechanisms. One is by breaking of the materials and the other is agglomeration of the molecules. Therefore the atmospheric aerosols can be considered as primary or secondary depending on whether the particles
are produces directly or indirectly. The primary aerosols are produced due to direct emission of particulate material into the atmosphere mostly from natural origin such as volcanic eruptions, wind blown dust, sea spray etc. and anthropogenic production. Secondary aerosol or indirect sources are the atmospheric layers, in which chemical reactions take place and convert the available natural and man-made atmospheric trace gases into solid and liquid particles.

1.3 Aerosol composition and its sources

Besides the size of aerosols the composition plays a crucial role in the potential effects of aerosols. The composition of aerosols is controlled by their origin and the physical and chemical processing, which they undergo in the atmosphere. A distinction can be made between primary and secondary aerosols. Primary aerosols are emitted directly into the atmosphere, whereas secondary aerosols are products of chemical reactions in the atmosphere. Due to processes as condensation and coagulation these primary and secondary aerosols will partially or completely be mixed in the atmosphere, which makes it difficult to classify aerosol according to this definition.

Main sources of aerosols:

<table>
<thead>
<tr>
<th>Natural</th>
<th>Anthropogenic</th>
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<tbody>
<tr>
<td><strong>Primary</strong></td>
<td><strong>Primary</strong></td>
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<tr>
<td>Mineral aerosol</td>
<td>Industrial dust</td>
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<tr>
<td>Sea salt</td>
<td>Soot</td>
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<tr>
<td>Volcanic dust</td>
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<tr>
<td>Biological debris</td>
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<td><strong>Secondary</strong></td>
<td><strong>Secondary</strong></td>
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<tr>
<td>Sulfates from biogenic gases</td>
<td>Sulfates from SO$_2$</td>
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<td>Sulfates from volcanic SO$_2$</td>
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<tr>
<td>Organic aerosols from Biogenic VOCs (Volatile Organic Compounds)</td>
<td>Organic aerosols from VOCs</td>
</tr>
<tr>
<td>Nitrates from NO$_x$</td>
<td>Nitrates from NO$_x$</td>
</tr>
<tr>
<td></td>
<td>Biomass burning</td>
</tr>
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Source: (Seinfeld and Pandis, 1998).
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1.3.1 Marine Aerosols

The oceans are one of the most important sources of atmospheric aerosols 1,000 - 10,000 Tg per year. This includes giant particles (>2-20 µm diameter) but these are not transported very far. Aerosols composed of sea salt originate from droplets ejected into the air when air bubbles burst at the ocean surface. Many small droplets are produced when the upper portion of an air bubble film bursts; these are called film droplets. Bubbles 2 mm in diameter each eject 100—200 film droplets into the air. After evaporation, the film droplets leave behind sea-salt particle. Hygroscopic salts NaCl (85%), KCl, CaSO₄, (NH₄)₂SO₄ account for ~3.5% of the mass of seawater. In addition, organic compounds and bacteria in the surface layers of the ocean are transported to the air by bubble bursting.

1.3.2 Biogenic Aerosols

Solid and liquid particles are released into the atmosphere from plants and animals. These emissions, which include seeds, pollen, spores, and fragments of animals and plants, are usually 1-250 µm in diameter. Bacteria, algae, protozoa, fungi, and viruses are generally <1 µm in diameter. Also oceans are an important source of biogenic aerosols. They are injected into the atmosphere by the bursting of air bubbles and by sea foam. Secondary biogenic aerosols are formed by gas to particle conversion of biogenic volatile organic compounds.

1.3.3 Mineral Aerosols

The transfer of particles to the atmosphere from the Earth’s surface is caused by winds and atmospheric turbulence. As these aerosols are made up of materials from the Earth’s crust, they are rich in iron and aluminium oxides and calcium carbonate. Generally larger sand grains become airborne, fly a few meters, and then land on the ground creating a burst of dust particles producing smaller particles. Most of the mineral aerosols in the air come originally from the desert regions. On the global scale, deserts (which cover about one-third of the land surface) are the main source of particles from the Earth’s surface. They provide 1,000-3,000 Tg per year of mineral particles.
1.3.4 Volcanic Aerosols

Volcanoes inject gases and particles into the atmosphere like fly ash. The large particles have short residence times, but the small particles produced by gas to particle conversion of SO$_2$ can be transported globally, particularly if they are blasted to high altitudes. Volcanic emissions play an important role in stratospheric chemistry.

1.3.5 Anthropogenic

The global input of particles into the atmosphere from anthropogenic activities is ~20% (by mass) of that from natural sources. The main anthropogenic sources of aerosols are dust from roads, wind erosion of tilled land, biomass burning, fuel combustion, and industrial processes. For particles with diameters >5 μm, direct emissions from anthropogenic sources denominate over aerosols that form in the atmosphere by gas to particle conversion (secondary particles) of anthropogenic gases. However, the reverse is the case for smaller particles, where gas to particle conversion is the overwhelming source of anthropogenically derived aerosols. About 35% of the aerosols in the atmosphere were sulfate, produced by the oxidation of SO$_2$ emissions. Particle emissions worldwide were dominated by fossil fuel combustion (primarily coal) and biomass burning.

1.3.6 In situ formation

In situ condensation of gases i.e. gas to particle conversion is important in the atmosphere. Gases may condense onto existing particles, thereby increasing the mass (but not the number) of particles, or gases may condense to form new particles. The former path is favored when the surface area of existing particles is high and the super saturation of the gases is low. If new particles are formed, they are generally <0.01 μm diameter. The quantities of aerosols produced by gas to particle conversion exceed those from direct emissions for anthropogenically derived aerosols, and they are comparable to direct emission in the case of naturally derived aerosols. Three major chemical species are involved in gas to particle conversion: sulfur, nitrogen, and organic and carbonaceous materials. Over the oceans the main source of sulfates derives from DMS. Sulfates are also produced in the vicinity of clouds by the combination of water molecules and
sulfuric acid molecules. Nitric acid can form from N₂O₅ in cloud water. Thus, evaporation of cloud water releases sulfate and nitrate particles into the air. Organic and carbonaceous aerosols are produced by gas to particle conversion from gases released from the biosphere.

1.4 Aerosol Transformation processes

There are different processes that transform aerosol particles of one size to another size range. The main aerosol transformation processes are coagulation, condensation of water vapor on existing particles and the processing of aerosols by non precipitating cloud cycles.

Individual aerosol particles combine together to form larger aerosol particles. This process is called coagulation, mainly caused by the random movements and subsequent collision and coalescence of aerosol particles. For very small particles, Brownian motion produces random movements are caused by small scale turbulence. Coagulation is mainly controlled by the diffusion coefficient of particles, which in turn is related to the particle mobility.

Condensation of water vapour takes place on the aerosols with increasing relative humidity and evaporation of water present on the aerosols takes place with decreasing relative humidity. Thus the aerosol particles grow as relative humidity increases and shrinks as relative humidity decreases. During the cycle of non precipitating clouds, aerosols large enough to act as cloud condensation nuclei grow because of condensation of vapours and agglomeration with smaller interstitial aerosols. During the evaporation of the cloud droplets the resulting dry aerosols would be much larger than initial one. Thus non precipitating clouds transfer aerosol mass from small particle range (r < 0.1 µm) to larger radius (r > 0.1 µm) range.

1.5 Aerosol Sinks Mechanism

On average particles are removed from the atmosphere at about the same rate as they enter it. Small particles can be converted into larger particles by coagulation. Since the mobility of a particle decreases rapidly as it increases in size, coagulation is essentially confined to particles less than 0.2 µm in diameter. Although coagulation does
not remove particles from the atmosphere, it modifies their size spectra and shifts small particles into size ranges where they can be removed by other mechanisms. Improvements in visibility that frequently follow periods of precipitation are due, in large part, to the removal (i.e. scavenging) of aerosols by precipitation particles. It is estimated that, on the global scale, precipitation processes account for about 80-90% of the mass of aerosols removed from the atmosphere. Aerosol particles less than 0.1 μm are collected most efficiently by diffusiophoresis. As precipitation particles fall through the air they collect particles greater than 2 μm in diameter with reasonable efficiency by impaction. Aerosols are also removed by impaction onto obstacles on the Earth’s surface. The terminal fall speeds of particles >1 μm diameter are sufficiently large that gravitational settling (i.e., dry fallout) is important as a removal process. For example, the fall speeds of particles 1 and 10 μm in diameter.

1.6 Properties of aerosols

Atmospheric aerosols have a direct effect on the radiation balance of Earth, climate change, air pollution (Seinfeld, J.H., 1989), fog formation, cloud properties (Kulmala et. al., 1996). Aerosol loading in boundary layer can cause the visibility degradation (Sloane, 1984, Sloane C.S. and White W.H., 1986) can directly affect the human health (Dockery et. al., 1993). To know the exact role and effects of aerosols in the atmosphere, it is necessary to study and analysis the physical and chemical properties of aerosols. The different properties of aerosols are classified as

1.6.1 Physical Properties

Aerosol size is one of the most important parameters in describing aerosol properties for characterization the physical behavior. The impact of aerosols is a function of size and chemical composition. The composition and size of aerosols are controlled by their sources and the physical and chemical processes, which they undergo in the atmosphere. The size of aerosols spans several orders of magnitude, ranging from several nanometres to hundreds of micrometers (Seinfeld and Pandis, 1998). The residence time of a particle in the atmosphere is strongly determined by the size and therewith the mass
of a particle. The aerosol size distribution is controlled by a complex system of physical processes as shown in figure 1.1.

Aerosols are classified into three modes by size range

1. Nucleation mode (fine particles) - < 0.1 μm
2. Accumulation mode (fine particles) - 0.1 μm – 1.0 μm
3. Coarse mode - > 1 μm

Figure 1.1: Idealized and simplified schematic illustration of atmospheric aerosols. Principal modes, sources, and particle formation and removal mechanisms are indicated ("Atmospheric Physics and Chemistry", Seinfeld and Pandis, 1998).
New particles in the atmosphere originate from emissions, mostly at the earth's surface, and through nucleation (homogeneous) of low vapour pressure gases, for example sulphuric acid. These processes are the main source for particles in the nucleation and aitken mode, i.e. those particles smaller than 0.1 nm. Coagulation is the main sink for nucleation and aitken mode particles, and a source of material for the accumulation mode particles. In this mode, 0.1 - 1.0 μm, the life time of aerosols is largest. Coagulation with larger particles from the coarse mode is due to their limited mobility very unlikely to occur and is therefore a negligible sink. The removal of particles by dry deposition is also inefficient in this size range, causing the accumulation of mass in this mode. The main loss for these aerosols is rain out, which causes the particles to have a lifetime of several days to weeks. Particles in the coarse mode are mainly emitted from the earth's surface and consist mostly of natural components with a crustal, marine or volcanic origin. Also biological sources contribute to this mode, e.g. pollen. Emissions are caused by the natural forces, e.g. the wind, or by anthropogenic activities such as traffic entrainment of paved and unpaved roads, agricultural operations, construction etc.

1.6.2 Optical Properties

Mie theory describes the scattering and absorption of electromagnetic radiation by spherical particles through solving the Maxwell equations. Mie theory is also called Lorenz-Mie theory or Lorenz-Mie-Debye theory. The Key assumptions in this theory are particle is a spherical and homogeneous therefore it is characterized by a single refractive index $m = n - ik$ at a given wavelength. Mie theory requires the relative refractive index that is the refractive index of a particle divided by the refractive index of a medium. For air $m$ is about 1, so one needs to know the refractive index of the particle (i.e., refractive index of the material of which the particle is composed).

If a particle has complex chemical composition such as some atmospheric aerosols, the effective refractive index must be calculated at a given wavelength. Mie theory calculates the scattered electromagnetic field at all points within the particle and at all points of the homogeneous medium in which the particle is embedded. For all practical applications in the atmosphere, light scattering observations are carried out in
the far-field zone (i.e. at the large distances from a particle). The air pollution haze is a
diverse mixture of various sizes and chemical species. Therefore to determine the
absorption and scattering coefficients of the mixture it is necessary to predict the
coefficients of each chemical species.

1.6.3 Chemical Properties

The coarse particles are predominantly comprised of sea salt, soot, and inorganic
crustal material, and tend to be basic rather than acidic. Over land crustal material may
dominate. Over sea, water evaporates from droplets produced by sea spray leaving salts
rich in Cl, Na, SO$_4^{2-}$ and Mg. Most of the elements in sea salt aerosols are relatively inert
and can be used to determine the fraction of sea salt in the sample. However, Cl is not
conservative as it has been shown to react with nitrogen dioxide as well as sulphuric and
nitric acids. The elemental composition of coarse particles is conserved during transport
except for chloride, bromide and iodide as well. Chemical reactions with Cl take place
on the surface of solid aerosol particles or in the solution surrounding them and create
gaseous products.

For example NO$_2$ reacts with sodium chloride to produce nitrosyl chloride (NOCI), a gas
and sodium nitrate (NaNO$_3$), a salt.

$$2\text{NO}_2(g) + \text{NaCl(s)} \rightarrow \text{NOCI(g)} + \text{NaNO}_3(s)$$

Another possible reaction is the oxidation of NO2 to nitric acid which then reacts to form
NaNO$_3$.

$$\text{HNO}_3(aq) + \text{NaCl(s)} \rightarrow \text{HCl(g)} + \text{NaNO}_3(s)$$

Gas phase compounds can escape from the aerosol, changing its composition.

The fine aerosol particles, which are largely made up of organic matter, sulphate
and nitrogen compounds. Organic matter in the fine aerosol fraction is formed from the
condensation or coagulation of VOCs that are produced from combustion processes or
from natural sources. Sulphate in fine particles is often derived from the oxidation of
sulfur dioxide. Gas phase and liquid phase oxidation of sulfur dioxide takes place in the
atmosphere. Oxidation of sulfitic (SO$_3$) and bisulfitic to sulphate (SO$_4^{2-}$) are slower
reactions that depend upon the presence of other oxidants such as iron or hydrogen
peroxide. Nitrate (NO$_3$) is produced from the oxidation of NOx, as the oxidation again
takes place by the hydroxly radical and the products are nitrate (NO₃) and nitric acid (HNO₃). Ammonia (NH₃) is released by the decay of organic matter and acts to neutralize 22% of the atmospheric acids. Nitrate and sulphate both contribute to “Acid Rain”, through the formation of sulfuric and nitric acid when dissolved in rainwater.

The increasing importance of aerosols in understanding the environmental processes as well as the use of aerosol technologies has led to a great interest in aerosol chemical characterization. The chemical properties include the chemical compositions of gas phase, single particle or group of particles and microstructure of the particles. The particles like fly ash carries toxic enriched compounds at surface while the nucleus is inert. The aqueous droplet may pick the surface active organic constituents from surrounding atmosphere. These compounds may influence the phase transfer of reactive gases like SO₂ or NH₃ into an aqueous solution (Daumer et al., 1987 and Niessner et al., 1988).

1.7 Role of aerosols in the atmosphere

1.7.1 Aerosol and Radiation budget

The atmospheric content of the greenhouse gases such as CO₂, CH₄ and O₃ is increasing which leads to an increase in surface temperatures and atmospheric aerosol content because of human interventions. All these reasons to change the radiation budget are causing climate change. Climate change is not only global average heating or cooling, but also is the changes in the ecosystem (Houghton et al., 2001).

The greenhouse gases reflect warming of the lower atmosphere, but aerosols play an important in climate change. Aerosols may directly interact with light and indirectly due to interactions with clouds. The direct effect is the scattering and absorption of incoming solar radiation by aerosols. The direct effect, which can force cooling of the atmosphere and may regionally counterbalance the positive forcing by greenhouse gases (Kiehl and Briegleb, 1993; IPCC, 2001).

Indirectly, more aerosols can lead to more cloud droplets. This leads to the smaller cloud droplets since the cloud water is shared between more numbers of drops. Smaller cloud droplets scatter sunlight more efficiently. The lifetime of smaller droplets
is longer. It takes more time to grow in raindrop size. Ultimately longer lifetime of cloud
leads absorption of short wave and so the increased number of aerosols will have a
cooling effect (Twomey, 1977, Albrecht 1989). The semi-direct effect had a warming
influence on climate because low clouds have a high albedo but do not significantly
reduce outgoing longwave radiation. The term ‘semi-direct effect’ was coined by
(Hansen et al., 1997) to describe the impact of absorbing aerosols on clouds. A series of
experiments with a simple Global Climate Model (GCM) showed that shortwave
absorption reduced low cloud cover by reducing relative humidity.

1.7.2 Climate change
Throughout the 20th century, it has been acknowledged that humans can influence
the atmospheric content of other greenhouse gases such as CH₄ and O₃. Increasing green
house gases leads to an increase in surface temperatures. Humans can also influence the
atmospheric radiative balance through changing e.g. surface albedo, or atmospheric
aerosol content. The last 30 years, radiative forcing due to aerosols has received much
attention in the scientific community. A large part of the key to understanding climate
change lies in understanding the atmospheric radiative balance. However, climate change
is not only global average heating or cooling, but also e.g. changed precipitation patterns,
circulation changes (both in atmosphere and ocean) and ecosystem changes (Houghton et.
al., 2001).

1.7.3 Ecosystem
Terrestrial ecosystems also modulate aerosols, such as dust and biogenically
derived particles. Biogenic and other aerosols, which incorporate organic material, can be
effective cloud condensation nuclei (CCN) and, thus, influence microphysical and optical
properties of clouds. Likewise, cloud properties affect the quantity and type of biogenic
aerosols in the atmosphere. Changes in cloudiness, cloud optical properties, precipitation,
and other meteorological variables directly control the emission and formation of
biogenic aerosols by altering the availability of radiation for photosynthesis and by
altering temperature. By affecting vapor pressure, temperature also determines the phase
distribution of some biogenic aerosols.
1.7.4 Health effects

Fine air particulate matter and traffic-related air pollution are correlated with severe health effects, including enhanced mortality, cardiovascular, respiratory, and allergic diseases (Bernstein et. al. 2004, Gauderman et. al. 2004, Samet et. al. 2005). The biochemical mechanisms and molecular processes that cause the toxicological effects such as oxidative stress and inflammatory response have not yet been resolved. Among the parameters and components potentially relevant for aerosol health effects are the specific surface, transition metals, and organic compounds (Bernstein et. al. 2004).
1.7.5 Atmospheric chemistry

Aerosols play a major role in atmospheric chemistry. Aerosols affect the amount of radiation and therefore photochemical reactions. There with photolysis rates of chemical species due to scattering and absorption of light (He and Carmichael, 1999). In addition, aerosols act as a catalyst or platform for reactions to occur i.e. a surface on which reactions may occur, which do not occur or are very slow in the gas phase. Aerosols also affect atmospheric chemistry by transport of semi-volatile compounds and may even act as a source for gases. An example is the reaction of N$_2$O$_5$ and nitric acid with sea salt. In this reaction reactive chlorine is liberated, which may have important implications for the halogen cycle and oxidation processes in the marine atmosphere (Andreae and Crutzen, 1997). Finally, aerosols play an important role in cloud chemistry by affecting the pH of cloud water.

1.8 Air Pollution and its effects

Air is essential to life, but pollution of it can be detrimental to our health. Polluted air contains substances that can be harmful to health, quality of life or the environment. Air pollution can be as obvious as bonfire smoke, but in many cases has no smell and cannot be seen. Technically, Air Pollution may be defined as any atmospheric condition in which substances (any natural or man-made chemical elements or compounds capable of being airborne) are present at concentrations high enough above their normal ambient levels to produce a measurable effect on humans, animals, vegetation, or materials. These substances may exist in the atmosphere as gases, liquid drops, or solid particles.

The major pollutants of concern from health and environmental perspective are:

1. Sulfur compounds: These include Sulfur Dioxide (SO$_2$), Hydrogen sulfide, and Sulfates (SO$_4^{2-}$) along with Carbonyl Sulfide, Carbon Disulfide and Dimethyl Sulfide. The major sources of sulfur dioxide are combustion of fossil fuels and organic matter, while the sulfides are mostly of biogenic / marine origin. The sulfates are formed on interaction of the gases with moisture and other atmospheric constituents. These gases have respiratory effects and can even cause permanent lung damage. Sulfur dioxide interacts with atmospheric moisture to form 'acid rain' which can causes widespread
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Health, plant and property damage. Sulphur attack can result in the formation of gypsum (Smith et. al. 2003), ettringite (Böke, H. and Akkurt, S., 2003) and thaumasite (Aguilera et. al. 2000).

2. Nitrogen compounds: These include Nitrous oxide (N\textsubscript{2}O), Nitric Oxide (NO), Nitrogen dioxide (NO\textsubscript{2}), Ammonia (NH\textsubscript{3}) and salts of Nitrate – NO\textsubscript{3}⁻, NO\textsubscript{2}⁻ and NH\textsubscript{4}⁺. The nitrous oxide is emitted totally by natural sources, principally by bacterial action in the soil and is a major 'greenhouse' gas. Nitric oxide is emitted principally during lightning and the burning of fuels at high temperature. It is photo-chemically reactive and interacts with other atmospheric components to form particulates and smog. Nitrogen dioxide is also emitted due to combustion and interacts with the atmospheric moisture to form “acid rain”. Ammonia is mainly emitted by biogenic processes and a few chemical industries. It can interact with the atmospheric components including NOx to form ammonium particles.

3. Carbon Monoxide (CO): This is a colourless and odourless gas formed as a result of incomplete combustion of fuels. It can be produced indoors from cooking stoves (using biofuel), wood-based heaters, etc and outdoors mainly from internal combustion engines of vehicles due to short residence time of fuels and low oxygen levels. It is a highly toxic gas affecting the oxygen uptake capacity of blood and is lethal in high concentration.

4. Ozone: While ozone at the stratospheric levels is essential for protecting us from ultraviolet rays, ground level ozone (O\textsubscript{3}) is a highly reactive oxidizing agent formed indirectly by the action of sunlight on NOx. It is a major constituent of smog and can cause severe health effects including breathing problems, reduced lung function, asthma, eye irritation, reduced resistance infections and even aging of lung tissue. Ozone can damage plants and trees leading to lower crop yield and also have capacity to damage rubber, fabrics, etc.

5. Suspended Particulate matter (SPM): SPM is a complex mixture of inorganic and organic substances. Particles less than 10 μm in diameter (PM\textsubscript{10}) and those less than 2.5
μm (PM$_{2.5}$) are thought to be potentially most harmful. Particles are directly emitted from sources such as non-nuclear power stations, motor vehicles, cement factories and open-cast coal mines. They also occur naturally as airborne spores and pollen grains. In urban areas motor vehicles, particularly diesel powered vehicles are a major source contributing an estimated 20-50% of the urban PM$_{10}$. The very small particulates are commonly called aerosols. Aerosols are suspensions of finely divided liquid or solid particles in gases. They can be formed by the conversion of gases to particles, by the disintegration of larger assemblages of solids or liquid or from biological sources like pollen, spores, microbes, etc. They can reach the stratosphere, where they may significantly alter the radiation and thermal budgets of the atmosphere and so produce significantly cooler temperatures at the earth's surface. They can also serve as condensation nuclei for the formation of clouds, which in turn affect the radiation balance. Tropospheric airborne particles may cause or exacerbate human respiratory illnesses. The health effects are independent of particle composition, particularly for very finely divided particles. Aerosols can reduce visibility due to their particle size.

6. Lead: The main sources of lead in air are petrol-engine vehicles (from lead tetraethyl in the gasoline) and non-ferrous metal smelting processes. It is a toxic metal and can go on accumulating in human tissues, causing brain and nervous system damage, along with digestive and kidney related diseases. Children seem to be at higher risk for the effects. While lead in petrol is being phased out over the world, its usage in metallurgical industries and manufacture of batteries is prevalent.

The other metal pollutants like Lead are Arsenic, Cadmium, Cyanide and Mercury. Arsenic mainly occurs in insecticides, fungicides and herbicides. Cadmium generally found in nature in association with Zinc. Cyanide occurs in seed of fruits such as apples, apricots, cherries and peaches. It is released in atmosphere by enzymatic or acidic hydrolysis. HCN is main source which is used as fumigating agent to destroy rodent in grain bins, buildings and also used in chemical syntheses and metal cleaning industries. While mercury occurs as trace component of many minerals and soil.
The phenomena involved in air pollution are complex. Once emitted into the atmosphere, primary pollutants are transported by wind, turbulence and diffusion can undergo chemical reaction or change phase to form secondary pollutants. Health and environmental impact of secondary pollutants can be more severe than their emitted precursors.

1.9 Air Pollution Meteorology

A close relationship exists between air pollution and certain atmospheric conditions like heat, temperature, wind etc. The transformation of an airborne pollutant, its movement with the prevailing winds (transport), its crosswind and vertical movement due to atmospheric turbulence (dispersion), and its removal amounts due to dry and wet deposition are influenced largely by the meteorological and environmental conditions. The meteorological parameters significant in air pollution are wind, radiation and atmospheric stability.

1.10 Chemical Characterization of Aerosols

The chemical characterization of aerosol is of great importance in understanding of environmental processes. The use of advanced aerosol technologies has led to interest in chemical characterization. The effect of aerosols on human health as atmospheric pollutants and other aspects like atmospheric chemistry are the central topics in the environmental research. Precise and detailed study of the chemical compositions of aerosols represents a formidable analytical task. The collected samples carry the information of molecular compositions and traces of minor constituents. The compositions of particles can be uniform or very different depending on their origin and mixing (internally or externally) through atmospheric processes.

The common chemical studies of aerosols are being done by the aspect of air pollution. These studies comprises of analysis by extraction and measurement of ionic concentrations in the aerosols. Aerosols collected by High volume air sampler are analyzed for major water-soluble chemical components using Ion Chromatograph and Atomic Absorption Spectrophotometer. After the sampling, the filter papers are being extracted for water soluble chemical components (Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, NH\textsubscript{4}\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+})
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and Mg\[^{2+}\]). Chemical analysis of anions is carried out with the help of Ion Chromatograph. Atomic Absorption Spectrophotometer is used for the analysis of cations and NH\[^{4+}\] is analyzed using spectrophotometric method.

But these techniques are not able to give the exact molecular compositions present in the aerosol sample. It is possible with Laser Raman Spectroscopy, which is discussed and used for the chemical characterization of aerosols at different locations for this study.

1.11 Development of Raman Techniques for Chemical Characterization

Some of the currently available techniques for chemical characterization are discussed here. These techniques are based on combined applications of lasers and different types of spectrum like absorption, emission and scattering.

1. Laser induced aerosol fluorescence: Fluorescence occurs due to the excitation of molecular or atomic systems by absorption of photons. Depending upon the structure of the molecule there are various possible ways for the system to return to ground state other than fluorescence. Compared to other optical detection methods, fluorescence detection has low detection limits and is more selective.

2. Laser induced breakdown spectroscopy: The technique is based on plasma generated light emission. It is extremely sensitive method for monitoring airborne substances in molecular form or as aerosols. (Biswas et. al., 1987, Essien et. al., 1988).

3. IR Laser backscattering aerosol: A laser beam propagating through an aerosol produces absorption and scattering. To study aerosol properties the differential scatter (DISC) lidar system is an appropriate technique. The sulfuric acid and ammonium sulphate aerosol were measured using DISC (Wright et. al., 1977 and Mudd et. al., 1982). In this the characteristic differences in the infrared backscatter spectra of aerosols are used to identify the chemical composition of the substantial amplitude variation over a relatively narrow wavelength range.

4. Resonance-Enhanced Raman Scattering: Raman spectroscopy is conventionally performed with green, red or near-infrared lasers. The wavelengths are below the first electronic transitions of most molecules, as assumed by scattering theory. The situation changes if the wavelength of the
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Exciting laser within the electronic spectrum of a molecule. In that case the intensity of some Raman-active vibrations increases by a factor of $10^2$-$10^4$. This resonance enhancement or resonance Raman Effect can be quite useful.

5. **Surface-Enhanced Raman Spectroscopy (SERS):** Generally done on a substrate containing silver or gold. Surface plasmons of silver and gold are excited by the laser, resulting in an increase in the electric fields surrounding the metal. Gives large increase in the measured signal (by up to $10^{11}$), given that Raman intensities are proportional to the electric field.

6. **Spontaneous Raman Spectroscopy (SRS):** This technique is generally used to study changes in the Raman spectra of molecules due to the change in temperature.

7. **Hyper Raman:** This technique requires very high power, but allows the observation of vibrational modes which are normally undetected or silent.

8. **Optical Tweezers Raman Spectroscopy (OTRS):** Used to study individual particles and biochemical processes in single cells trapped by optical tweezers.

9. **Stimulated Raman Spectroscopy:** Uses a two color pulse transfers the population from ground to a rovibrationally excited state, if the difference in energy corresponds to an allowed Raman transition.

10. **Spatially Offset Raman Spectroscopy (SORs):** The Raman scatter is collected from regions laterally offset away from the excitation laser spot, leading to significantly lower contributions from the surface layer than with traditional Raman spectroscopy.

11. **Coherent anti-Stokes Raman spectroscopy (CARS):** Two laser beams are used to generate a coherent anti-Stokes frequency beam, which can be enhanced by resonance.

And the one we are using for this study is

12. **Laser Raman Spectroscopy:** Most simple and very interesting method of characterization of aerosols. Raman scattering results from an interaction of EM radiation with atoms or molecules. The scattered light with change in energy is Raman scattering. Due to induced dipole moment if vibration produces a change
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in molecular polarizability, a Raman spectrum can be observed. The first Raman spectra of aerosol particles trapped in an electrostatic particle levitation cell using an Argon ion laser and double monochromator were published by (Fung K.H. and Tang I.N., 1988a, 1988b).

1.12 Applications of Raman Spectroscopy

Raman spectroscopy provides valuable structural information about materials. When laser light is incident upon a sample, a small percentage of the scattered light may be shifted in frequency. The frequency shift of the Raman scattered light is directly related to the structural properties of the material. A Raman spectrum provides information that is a unique to the material.

Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules. It therefore provides information by which the molecule can be identified. Another way that the technique is used to study changes in chemical bonding. In solid state physics, spontaneous Raman spectroscopy is used to characterize materials, measure temperature, and find the crystallographic orientation of a sample. A solid material has characteristic phonon modes with every single molecule that can help to identify it.

Raman scattering by an anisotropic crystal gives information on the crystal orientation. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to find the orientation of the crystal, if the crystal structure is known. Raman active fibers, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibers also exhibit similar shifts. The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes.

Raman spectroscopy is also employed in many other applications including mineralogy, pharmacology, corrosion studies, analysis of semiconductors and catalysts, in situ measurements on biological systems, and even single molecule detection. Applications will continue to increase rapidly along with further improvements in the technology.
1.13 Chemical applications of Laser Raman Spectroscopy

Laser Raman spectroscopy is widely used for the chemical studies as it is very useful in practical terms

1. The easy sampling of solids, powders, gels, liquids, slurries, and aqueous solutions i.e. no Special sample preparation is required.
2. Glass is almost completely transparent in the Raman so spectra can be readily obtained from samples in tubes and capillaries even by using fibers.
3. The sample can be any convenient shape and need not to be transparent to the laser radiation. In addition, only a small quantity of sample is sufficient.
4. Raman spectra are well resolved with high information content with access to the whole range of vibrational spectrum from 40 cm\(^{-1}\) to 4000 cm\(^{-1}\) can be obtained in one run on one instrument.
5. Remote sampling using fiber optic probes (up to 100 meters).

For chemical aspect Raman spectroscopy can be used to study wide range of organic compounds and can be compared with IR spectra to asses the potential of Raman spectroscopy as an analytical tool. Some of the preliminary conclusions are

1. Symmetric and pseudo-symmetric vibrations are strong in Raman. These are weak or absent in infrared. Therefore the vibrations such as C=C, C≡C, S=S, N=N etc. are readily observed.
2. The nitrile stretching vibration is always strong in Raman, whereas the nitrile group frequency is of variable intensity and very weak in infrared.
3. C=S and S-H are relatively strong in the Raman, whereas the latter is virtually undetectable in the infrared.
4. C-H and N-H vibrations can be studied using Raman without the tremendous interference, but the O-H group vibrations are weak in Raman compared to these two groups.
5. Aromatic compounds have particularly strong spectra.
The quantitatively analysis can give the amount of compound giving rise to Raman lines. Raman Spectroscopy permits the chemical characterization of broad variety of environmentally significant materials existing within the aerosol in the form of organic and inorganic species (Harpale et. al., 2006).

Aerosol Raman Spectroscopy is less studied, hence we attempt to undertake this work to throw light on molecular structure of aerosols using this advanced technology. As Raman shift is a property of the particular molecule (Schweiger, 1990), Raman Spectroscopy is an ideal tool for investigating chemical composition of aerosol particles (Escribano et al., 2001). There are several studies of single aerosol particles, pollen grains (Ivleva et al., 2005) and on detection of bioaerosols relation with human health (Spurny, 1994; Lacey and Dutkiewicz, 1994). The main emphasis of the research work carried out is to characterize the aerosols to understand their presence and the chemical effects in the atmosphere. This study is useful mainly for air pollution and radiation balance in the atmosphere.