Chapter One: Atmospheric Aerosols

1.1 Introduction

Atmospheric aerosols have significant local, regional and global impacts. Local impacts include vehicular emissions, wood burning fires and industrial processes that can lead to urban air pollution [*Fenger, 1999; Mayer, 1999*] and possible adverse health effects [*Dockery et al., 1993; Harrison and Yin, 2000; Pope et al., 2002*]. Regionally, aerosols can be transported from areas of high emissions to relatively clean remote regions. Aerosols have the potential to significantly influence our entire planet through their role in heterogeneous chemistry in the troposphere and stratosphere [*Ravishankara, 1997; Finlayson-Pitts and Pitts, 2000*], as well as their effect on the Earth's climate as they scatter sunlight and serve as condensation nuclei for cloud droplet formation [*Charlson et al., 1992; Penner et al., 2001; Ramanathan et al., 2001*]. At present, the radiative effects of aerosols have the largest uncertainties in global climate predictions to quantify climate forcing due to man-made changes in the composition of the atmosphere. A better understanding of the formation, composition and transformation of aerosols in the atmosphere is of critical importance in order to better quantify these effects.

The word aerosol was introduced more than 80 years ago as an analogy to the term hydrosol, a stable liquid suspension of solid particles [*Hinds, 1999*]. An aerosol is defined in its simplest form as solid or liquid particles suspended in a gas, and it includes a wide range of phenomena such as dust, fume, smoke, mist, fog, haze, and smog [*Seinfeld and Pandis, 1998*]. Atmospheric aerosols are generally considered to be particles that range in size from a few nanometers (nm) to tens of micrometers (μm) in diameter. Particles may be either directly emitted into the atmosphere or formed there by the oxidation of precursor gases, such as sulphur dioxide, nitrogen oxides and volatile organic compounds (VOCs), where the resulting oxidation products nucleate to form new particles or condense on pre-existing ones. Particles formed through these two routes are referred to as primary and secondary particles, respectively [*Finlayson-Pitts and Pitts, 1997; Seinfeld and Pandis, 1998*]. Particles in the atmosphere arise from natural sources as well as anthropogenic activities [*Seinfeld and Pandis, 1998*]. The former source includes windborne dust, sea spray, volcanic activities and biomass burning, while emissions of particles attributable to the activities of humans arise primarily from four source categories: fuel combustion, industrial processes, nonindustrial fugitive sources (e.g. construction work), and transportation sources (e.g. automobiles). Natural aerosols are probably 4 to 5 times larger than anthropogenic ones on a global scale, but regional variations in man-made pollution may change this ratio significantly in certain areas, particularly in the industrialised Northern Hemisphere [*Seinfeld and Pandis, 1998*].

Once airborne, particles can change their size and composition by condensation of vapour species or by evaporation, by coagulation with other particles, by chemical reaction, or by activation in the presence of water supersaturation to become fog and cloud droplets. Particles are eventually removed from the atmosphere by two mechanisms: deposition at the Earth's surface (dry deposition) and incorporation into cloud droplets during the formation of precipitation (wet deposition). Because wet and dry deposition lead to relatively short residence times in the troposphere, and because the geographical distribution of particle sources is highly nonuniform, tropospheric aerosols vary widely in concentration and composition over the Earth. Whereas atmospheric trace gases have lifetimes ranging from less than a second to a century or more, residence times of particles in the troposphere vary only from a few days to a few weeks [*Seinfeld and Pandis, 1998*].

1.2 Relevance of atmospheric aerosols

Anthropogenic emissions of atmospheric aerosol and their precursors have increased dramatically over the past century and have been implicated in many areas ranging from human health to climate change [*Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000*]. The degradation of visibility is perhaps the most visible aspect of urban and regional air pollution to the public. Aerosol particles in the size range of 0.1 – 1.0 μm are major contributors to this phenomena because of their highly efficient light scattering properties [*Horvath, 1995; Seinfeld and Pandis, 1998; Cheng and Tsai, 2000*]. Aerosols also can act as sites for heterogeneous chemical reactions to take place [*Ravishankara, 1997*]. The most significant of these reactions are those that lead to the destruction of the stratospheric ozone. 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 [*Solomon et al., 1986; Molina, 1991*]. In addition to visibility and heterogeneous chemistry implications, the effects of atmospheric aerosols on human health and global climate have been increasingly recognised.

1.2.1 Effects of atmospheric aerosols on air quality and human health

The impact of gaseous and particulate pollutants is gauged by the effect on pollution receptors. For example, deposition of acidic pollutants can speed up the deterioration of building materials, harm vegetation, damage the aquatic ecosystem, cause breathing problems and even increase the mortality rate among humans [*Seinfeld and Pandis, 1998*]. Air pollution has a long history [*Brimblecombe, 1987; Bowler and Brimblecombe, 1992*]. From at least the 13th century up to the mid-20th century, documented air pollution problems were primarily associated with high concentrations of sulphur oxide gases and soot particles [*Noble and Prather, 1998*]. This type of pollution is often referred to as “London Smog” because of a severe pollution episode in that city in December 1952, which led to over 4000 deaths. Moreover, the discovery of photochemical air pollution in the Los Angeles area in the mid-1940s have made high concentrations of ozone and photochemical products and their associated impacts on human health a major issue worldwide [*Finlayson-Pitts and Pitts, 2000*].

Air quality standards for particulate matter in countries such as the United States were expressed some years ago in terms of the mass of total suspended particulate matter (TSP). The standard was then changed to mass of suspended particulate matter less than 10 μm in size, commonly called PM_{10}, and more recently was modified to include particulate matter less than 2.5 μm in diameter $PM_{2.5}$ [*EPA, 1997*]. The rationale for basing air quality standards on smaller particles relied on the fact that they can penetrate deeper into the lung and hence their potential adverse health effect is much greater [*Phalen, 1984*]. In addition, they have larger surface-to-volume ratios and are commonly produced from gas-to-particle conversion or combustion processes, which are known to produce carcinogens such as polycyclic aromatic hydrocarbons. Many epidemiological studies have observed associations between particulate air pollution and human health [*Dockery et al., 1993; Pope et al., 1995*]. An increase of 1.5% in the total daily mortality with an increase of 10 µg m^{-3} in $PM_{2.5}$ concentration has been reported [*Schwartz et al., 1996*]. Daily time-series studies have observed associations between daily mortality and changes in particulate air pollutions [*Schwartz and Dockery, 1992; Schwartz, 1994*]. Elevated particulate air pollution has been associated with declines in lung function and increases in respiratory symptoms [*Dockery et al., 1989; Pope et al., 1991; Pope and Dockery, 1992; Pope et al., 2002*]. Fine particulate pollution was associated with lung cancer and cardiopulmonary mortality [*Dockery et al., 1993; Pope et al., 1995; Schwartz et al., 1996; Pope et al., 2002*]. Each 10 µg m^{-3} elevation in fine particulate air pollution was associated with approximately a 6%, and 8% increased risk of cardiopulmonary and lung cancer mortality, respectively. On the other hand measures of coarse particle fraction and total suspended particles were not consistently associated with mortality [*Pope et al., 2002*].

It is widely believed that in the short term air pollution only anticipates unavoidable deaths. Recent studies have shown, however, that this is not the whole story, and that when air pollution increases, the excess mortality due to the anticipated deaths of particularly vulnerable people -called harvesting- is not followed by a deficit [*Schwartz, 2001; Zanobetti et al., 2002*]. This implies that air pollution not only kills people in a "high risk pool", but also recruits new individuals to that pool. This is consistent with the results of a recent study, which showed that short-term inhalation of fine particulate air pollution and ozone at concentrations that occur in the urban environment causes acute conduit artery vasoconstriction in healthy adults [*Brook et al., 2002*].

Currently, there are too many plausible mechanisms and too few established facts to explain these epidemiological studies [*Donaldson and MacNee, 1998; Harrison and Yin, 2000*]. What is particularly interesting from a chemical point of view, however, is that most of the cities included in the studies above are quite disparate in terms of location and the type of air pollutants that would be expected to predominate in each region, yet a consistent relationship between adverse health effects and particulate pollution is found. This suggests either that there is a general inflammatory response to inhalation of such particles, which is independent of their specific chemical composition or that there are some common chemical components responsible for the effect. The UK Department of Health Committee on the Medical Effects of Air Pollution concluded that no known chemical substance is of sufficient toxicity given the current level of exposure to particulate matter to explain the observed magnitude of health effects [*Department of Health, 1995*].

It is difficult, however, to imagine that chemical composition does not play a role. Chemical components of atmospheric particles are highly diverse. They range from near neutral and highly soluble substances such as ammonium sulphate, ammonium nitrate and sodium chloride through sooty particles made up largely of elemental carbon coated in organic compounds, and essentially insoluble minerals such as particles of clay. Evidence is being presented that trace metals influence the toxicity of airborne particulate matter. Such evidence derives from the toxicological rather than the epidemiological studies and depends mechanistically on the idea that metals are redox-active and can, therefore, induce or catalyse chemical change leading to production of free radicals such as the hydroxyl radical, which have a known ability to cause tissue inflammation. In addition, toxicological studies found that ultrafine particles of less than 100 nm appear to have considerably enhanced toxicity per unit mass and that their toxicity increases as particle size decrease [*Donaldson and MacNee, 1998*]. This may be explained either through a greater surface area per unit mass if the toxic components reside solely or partially in the surface of the particles, or via the ability of ultrafine particles to penetrate the pulmonary interstitium [*Seaton et al., 1995*]. *Siegmann et al.*, [*1999*] suggested that particles with a diameter below 1 μm act as vehicles transporting toxic chemicals into the human respiratory system. Such findings and suggestions are interesting, but yet far from conclusive. One of the major issues is whether the toxicity of the particles resides in some particular fraction of the particles as defined by the chemical composition, particle size, or surface reactivity [*Harrison and Yin, 2000*].

1.2.2 The role of atmospheric aerosols in the global climate

In their most recent report, the Intergovernmental Panel on Climate Change (IPCC) concluded that emissions of greenhouse gases and aerosols due to human activities continue to alter the atmosphere in ways that are expected to affect the climate [*IPCC, 2001*]. For a while, it looked simple: greenhouse gases warm the Earth and sulphate aerosols cool it down [*Charlson et al., 1992*]. Because aerosol particles in the atmosphere scatter sunlight back into space, they reduce the amount of energy that the planet absorbs, keeping it cooler. But this simplistic view ignored the fact that aerosol particles in the real world may also lead to heating of the lower atmosphere if they contain light absorbers such as elemental carbon and mineral dust [*Andreae, 2001*]. In fact, it was proposed that the warming effect from black carbon in aerosols may balance the cooling effect of the sulphate component, the largest single contributor to aerosol cooling [*Jacobson, 2001*]. Scattering and absorbing the solar radiation is known as the "direct" effect of aerosols on the global climate, which can lead to either cooling or warming of the atmosphere depending on the proportion of light scattered to that absorbed.

Aerosols also have an "indirect" effect on climate by altering the properties of clouds, resulting in a change of their scattering properties and longevity [*Penner et al., 2001*]. Indeed, if there were no aerosols in the atmosphere, clouds would be much less common. It is very difficult to form cloud droplets without small aerosol particles acting as "seeds" to start the formation of cloud droplets. According to theory [*Twomey, 1974; Twomey, 1977*], as aerosol concentration increases within a cloud, the water in the cloud gets spread over many more droplets, each of which is correspondingly smaller. This has two consequences: clouds with smaller droplets reflect more sunlight, and such clouds last longer, because it takes more time for small droplets to coalesce into droplets that are large enough to fall to the ground. The latter effect has been supported by certain observations indicating that aerosols from forest fires and urban pollution can suppress rain and snow fall [*Rosenfeld, 1999; Rosenfeld, 2000*]. In this way, changing aerosol in the atmosphere can change the frequency of cloud occurrence, cloud thickness, and rainfall amounts. These changes in cloud droplets number concentration and size and their longevity are, respectively, known as the "first" and "second" indirect effects of aerosol on climate and they are both believed to increase the amount of sunlight that is reflected into space without reaching the Earth's surface, resulting in a cooling effect.

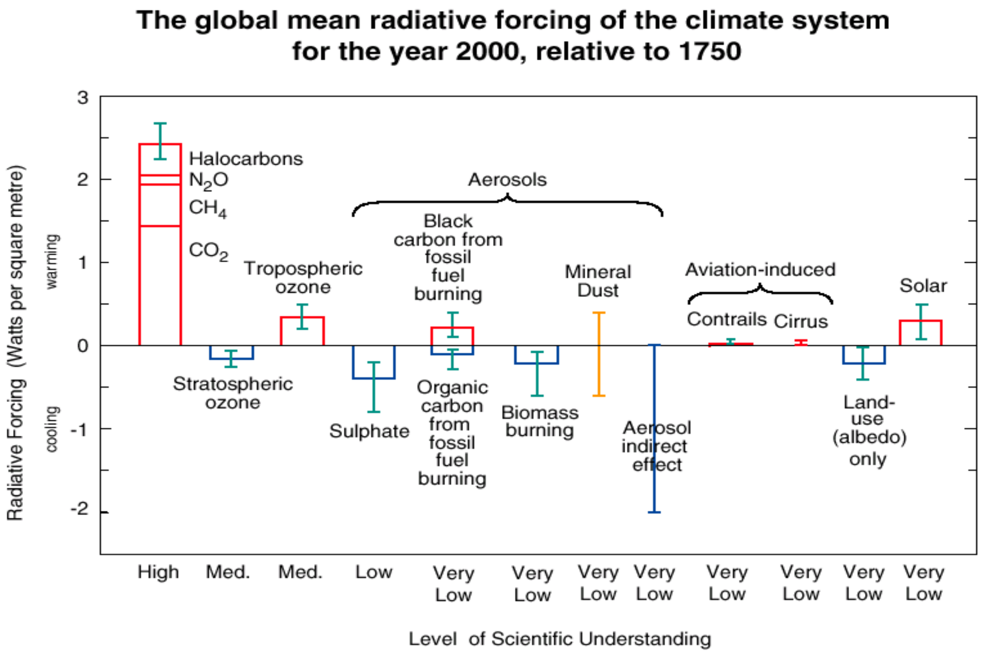

Figure 1.1: External factors and their estimated radiative forcing on the global climate system (source www.ipcc.ch)

Figure 1.1 summarises the state of scientific knowledge of the effects of various external factors on the global climate as reported by the Intergovernmental Panel on Climate Change [*IPCC, 2001*]. The figure presents the global, annual mean radiative forcings due to a number of factors for the period from pre-industrial time to a recent year (1750 – 2000). Radiative forcing is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system, and is an index of the importance of the factor as a potential climate change mechanism. It is expressed in Watts per square metre, W m^{-2} [*Penner et al., 2001*]. The heights of the rectangular bars denote central or best estimates of the contributions of these forces – some of which yield warming, and some cooling, while its absence denotes no best estimate is possible. The vertical line about the rectangular bars indicates a range of estimates, guided by the spread in the published values of the forcings and physical understanding. All the forcings shown have distinct spatial and seasonal features such that the global, annual means appearing on this plot do not yield a complete picture of the radiative perturbation. They are only intended to give, in a relative sense, a first-order perspective on a global, annual mean scale and cannot be readily employed to obtain the climate response to the total natural and/or anthropogenic forcing.

Some of the forcings possess a much greater degree of certainty than others. For example, because of their long lifetimes, the principal greenhouse gases (e.g. CO_2) are well mixed over the globe thereby perturbing the global heat balance. Aerosols, on the other hand, represent perturbations with stronger regional signatures because of their spatial distribution, which prevents a simple sum of positive and negative effects to be expected to yield the net effect on the global climate system. Models have been used to estimate the direct radiative forcing for five distinct aerosol species. The global annual mean radiative forcing is estimated to be –0.4 W m^{-2} for sulphate, -0.2 W m^{-2} for biomass burning aerosols, -0.1 W m^{-2} for fossil fuel organic carbon and +0.2 W m^{-2} for fossil fuel black carbon aerosols and in the range –0.6 to +0.4 W m^{-2} for mineral dust aerosols. The level of scientific understanding for sulphate aerosol is low while for biomass burning, fossil fuel organic carbon, fossil fuel black carbon, and mineral dust aerosols the level of scientific understanding is very low. The sign of the effects due to mineral dust aerosols is itself an uncertainty.

The indirect aerosol radiative forcing through their effect on clouds is believed to have a cooling effect, although of very uncertain magnitude. Models have been used to estimate the "first" indirect effect of anthropogenic sulphate and carbonaceous aerosols (namely, a reduction in the cloud droplet size at constant liquid water content) yielding global mean radiative forcings ranging from –0.3 to –1.8 W m^{-2}. The lack of best estimate for this effect is due to the large uncertainties in aerosol and cloud processes and their parametisations in models, the incomplete knowledge of the radiative effect of black carbon in clouds, and the possibility that the forcings of individual aerosols types may not be additive. The "second" indirect effect of aerosols (their effect on cloud lifetime, which is believed to also lead to a negative forcing) is conceptually important, but there exists very little confidence in the simulated quantitative estimates and therefore it is not shown in Figure 1.1.

It is clear from this summary that there is much less confidence in the ability to quantify the total aerosol direct and indirect effects on the global climate than that for the greenhouse gases. This is likely because the radiative forcing of aerosols differs from that of greenhouse gases in several important ways [*Charlson et al., 1992*]. Unlike greenhouse gases, aerosol particles are relatively short-lived in the troposphere, resulting in spatial and temporal nonuniformity of forcing. Aerosol forcing is greatest in daytime and in summer, whereas greenhouse gas forcing acts over the full diurnal and seasonal cycles. Furthermore, unlike molecular absorption, which is invariant from one molecule to the next for a particular species, the single-particle optical properties of aerosol particles depend on particle size and composition. Such differences make a description of the aerosol influences on climate much more complex than a treatment of the radiative influences of greenhouse gases. Aerosols have most likely made a significant negative contribution to the overall radiative forcing, but cannot be considered simply as a long-term offset to the warming influence of greenhouse gases.

In conclusion, scientists have much to learn about the way aerosols affect regional and global climate. We have yet to accurately quantify the relative impacts on climate of natural aerosols and those of human origin. Moreover, we do not know in what regions of the planet the amount of atmospheric aerosol is increasing, is diminishing, and is remaining roughly constant. Measurements of the spatiotemporal variations in the concentration of aerosol particles and their physical properties and chemical composition are essential to establish a fundamental, quantitative understanding of their direct sources, their formation from chemical reactions in the atmosphere, their fates, and how their physical and chemical properties determine their impacts on the global climate and human health.

1.3 Aerosol properties

1.3.1 Particle size definitions

Atmospheric particles are usually referred to as having a diameter, implying they are spherical. However, particles in the atmosphere have widely variable shapes for which geometrical diameters are often not meaningful. Some means of expressing the size of such particles is essential since many important properties of the particles such as volume, mass, and velocity depend on the size [*Hinds, 1999*]. In practice, the size of such irregularly shaped particles is expressed in terms of an equivalent diameter that depends on a physical, rather than a geometrical, property. An equivalent diameter is defined as the diameter of the sphere that would have the same value of a particular physical property as that of the irregular particle [*Hinds, 1999*].

There are different types of equivalent diameters. One of the most commonly used is the *aerodynamic diameter, D_a*, which is defined as the diameter of a sphere of unit density (1 g cm^{-3}) that has the same settling velocity in air as the particle under consideration. Aerodynamic diameter standardizes particles of various shapes and densities to spheres having the same aerodynamic property, settling velocity. The particle aerodynamic diameter D_a is given by Equation 1.1

$$D_a = D_g k \sqrt{\frac{\rho_p}{\rho_0}} \tag{1.1}$$

where D_g is the particle geometric diameter, ρ_p is the density of the particle, ρ_0 is the reference density (1 g cm^{-3}), and k is a shape factor, which is 1.0 in the case of a sphere. Because of the effect of particle density on the aerodynamic diameter, a spherical particle of high density will have a larger aerodynamic diameter than its geometric diameter. However, the density for most substances is less than 10 so that the difference between the geometric and aerodynamic diameters of a spherical particle is less than a factor of ~ 3.

It is important to note that various types of aerosol instrumentation report different measures of particle diameter depending on the employed methodology and application. Therefore, a universal measure of aerosol particle size does not exist and as a result the sizing definition will be specified for particle diameters reported in this thesis.

1.3.2 Particle size classification

Particle size is one of the most important parameters for characterising the behaviour of aerosols. The diameters of atmospheric aerosols span over four orders of magnitude, from a few nanometers to around 100 μm. To appreciate this wide size range one just needs to consider that the mass of a 10 μm diameter particle is equivalent to the mass of one billion 10 nm particles of the same composition. Atmospheric aerosols are normally classified into separate modes according to their size, formation process and atmospheric age. The exact size ranges of these modes vary in the literature, but the definitions described in this section will be used throughout this thesis.

Based on the number, surface, and volume distributions of aerosol particles shown in Figure 1.2, four distinct groups of atmospheric particles can be defined. Particles with diameters larger than 1.0 μm are identified as the *coarse* mode. These particles are mainly produced by mechanical processes and are introduced directly into the atmosphere from both natural and anthropogenic sources. The most significant source is the bursting of bubbles in the ocean, which creates coarse particles of sea salt. The wind also picks up dust, soil and biological particles and suspends them in the atmosphere. Anthropogenic coarse particles are introduced into the atmosphere through the abrasion of machinery, on the surface of roads, and in industrial and agricultural processes. Because of their relatively large size, coarse particles settle out of the atmosphere in a reasonably short time by sedimentation, except on windy days, where fallout is balanced by reentrainment.

Particles with diameters between 0.1-1.0 μm are considered as the *accumulation* mode representing a region of particle growth mainly due to the coagulation of particles with diameters smaller than 0.1 μm and from condensation of vapours onto existing particles, causing them to grow into this size range. They can also be introduced directly into the atmosphere, mainly through the incomplete combustion of wood, oil, coal, gasoline and other fuels. Because of the nature of their sources, particles in the accumulation size range generally contain substantial amounts of organic material as well as soluble inorganics such as ammonium, nitrate and sulphate. The *accumulation* mode is so named because particle removal mechanisms are least efficient in this regime, causing particles to accumulate there until they are ultimately lost through rain or other forms of precipitation (wet deposition).

The *Aitken* mode particles, extending from 0.01 to 0.1 μm diameter, are formed from ambient-temperature gas-to-particle conversion as well as condensation of hot vapours during combustion processes. These particles act as nuclei for the condensation of low-vapour pressure gaseous species, causing them to grow into the accumulation range. The lifetime of these particles is short, as they are lost principally by coagulation with larger particles. The Aitken and accumulation mode particles are referred to collectively as fine particles.

The final type of particles are those with diameters smaller than 0.01 µm (not shown in Figure 1.2) and are known as ultrafine particles. They are thought to be generated by gas-to-particle conversion processes that are not yet well understood on a molecular level. Because of their very small size and mass, they are difficult to study given the available measurement techniques. These particles have been observed in bursts of very large numbers in the presence of either biogenic or anthropogenic emissions under favourable local conditions in many different environments including forests [*Kulmala et al., 2004*] and coastal zones [*O'Dowd et al., 2002*] and have been referred to as the *nucleation* mode. These particles are only observed as a distinct mode at their source and have a very short lifetime, some times on the order of min, due to their rapid coagulation or random impaction onto surfaces.

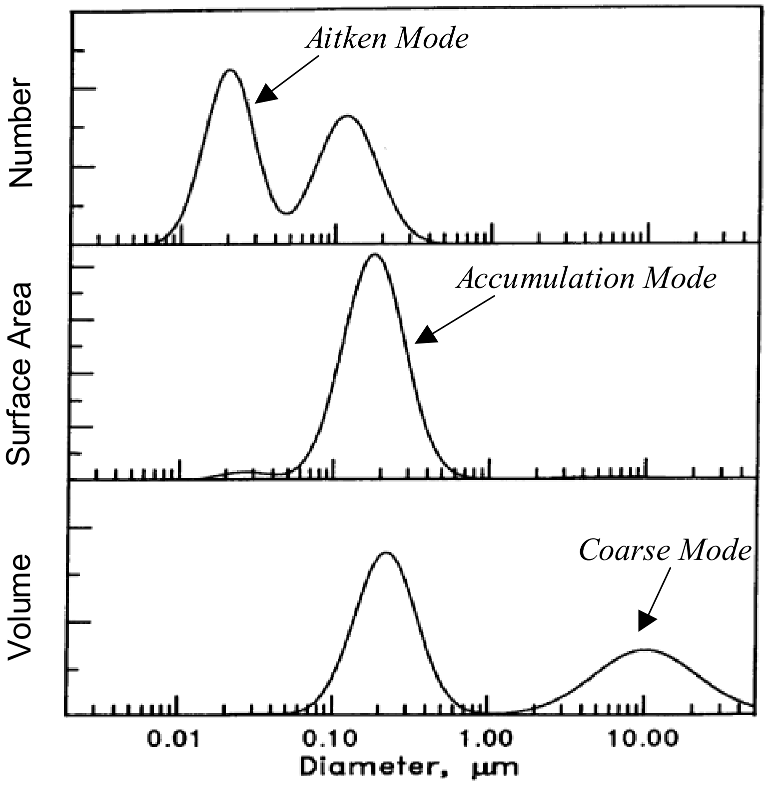

Figure 1.2: illustration of number, surface, and volume distributions for a typical urban model aerosol [Seinfeld and Pandis, 1998]

The nucleation and Aitken mode particles account for the majority of atmospheric particles by number, but due to their small sizes, they rarely account for more than a few percent of the total mass. Hence if the toxicological effects are determined primarily by the number of particles, rather than their mass, these small particles could ultimately prove to be of high importance. The Accumulation mode particles account, generally, for a significant fraction of the total aerosol mass and have the greatest surface area. This makes these particles of significant importance to gas phase deposition and atmospheric heterogeneous chemistry. Most of the aerosol mass is found in the coarse mode, where large particles contribute significantly to the optical properties of atmospheric aerosols. These modes, in general, originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, have different lifetimes, have different chemical composition, have different optical properties, and differ significantly in their deposition patterns in the respiratory tract. Therefore, the distinction between nucleation, Aitken, accumulation and coarse particles is a fundamental one in any discussion of the physics, chemistry, measurement, or health effects of aerosols.

1.3.3 Other aerosol properties

Many of the effects of atmospheric aerosols (e.g. radiative effect) depend on their chemical composition, which rarely consists exclusively of a single component. Atmospheric aerosols are generally composed of a mixture of species from a number of sources. The mixing state, i.e. how all the components are distributed among the particles, of these components is one of the important properties of atmospheric aerosols. In an aerosol population, particles are *externally* mixed if they arise from different sources and have different chemical composition. On the other hand, particles are *internally* mixed if all particles of a given size contain a uniform mixture of components.

The shape of an aerosol particle is another property. Particle shape can affect its surface area, aerodynamic behaviour and optical properties. Scanning electron microscopy (SEM) studies have shown that liquid atmospheric aerosol particles are nearly always spherical, but solid particles usually have variable shapes such as crystalline, aggregate, fractal and amorphous [*Hinds, 1999*]. Finally, aerosol concentration is most commonly reported in terms of mass or number of particles in a unit volume of aerosol. Common units are µg m^{-3} and number cm^{-3}, respectively. Mass concentration is equivalent to the density of an aerosol, but the latter term is not used in order to avoid confusion with particle density.

1.4 Aerosol chemical composition

Understanding the formation, composition and behaviour of ambient aerosol particles is of critical importance in order to better quantify the effects of aerosols on issues like human health and global climate. To date, the climatic impact of aerosol particles is poorly quantified, and the compounds that contribute to adverse health effects have not been established (see section 1.2). This is partly due to the fact that the chemical composition of ambient aerosol particles has not been fully characterised, in particular its organic fraction. Atmospheric aerosols are generally composed of variable amounts of sulphate, ammonium, nitrate, sodium, chloride, trace metals, crustal elements, water and carbonaceous material. The sulphate component is derived predominantly from the atmospheric oxidation of anthropogenic and natural sulphur-containing compounds such as sulphur dioxide (SO_2) and dimethyl sulphide (DMS), respectively. Nitrate is formed mainly from the oxidation of atmospheric nitrogen dioxide (NO_2). Sulphate and nitrate are initially formed as sulphuric (H_2SO_4) and nitric acids (HNO_3), but are progressively neutralised by atmospheric ammonia forming the corresponding ammonium salts. Chlorides also enter atmospheric particles as a result of ammonia neutralisation of hydrochloric acid (HCl) vapour, which is emitted from sources such as incinerators and power stations. But the main source of chlorides is sea spray even at locations hundreds of miles from the coast. Crustal materials include soil dust and windblown minerals. They vary in composition according to local geology and surface conditions and reside mainly in the coarse particle fraction.

The carbonaceous fraction of the aerosols consists of both elemental and organic carbon. Elemental carbon (EC), also called black carbon, graphitic carbon, or soot, is emitted directly into the atmosphere, predominantly from combustion processes. While particles containing organic carbon (OC) can be directly emitted into the atmosphere (i.e. from primary sources such as biomass burning and combustion processes), they can also be introduced by secondary organic aerosol (SOA) formation. The latter process occurs when volatile organic compounds undergo atmospheric oxidation reactions, forming products that have low enough volatilities to form aerosol via either nucleation or gas-to-particle partitioning to pre-existing particles [*Odum et al., 1996; Hoffmann et al., 1997; Kamens et al., 1999; Kamens and Jaoui, 2001*]. Volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic and biogenic sources [*Went, 1960; Odum et al., 1996; Seinfeld and Pandis, 1998; Kleindienst et al., 1999; Aschmann et al., 2002*]. Anthropogenic VOC sources comprise organics such as alkanes, alkenes, aromatics and carbonyls, while biogenic sources include organics such as isoprene, monoterpenes and sesquiterpenes. Aromatics as well as monoterpenes are particularly important constituents of urban and regional atmospheric chemistry and most have been identified as SOA precursors [*Odum et al., 1996; Griffin et al., 1999; Kamens et al., 1999; Larsen et al., 2001*].

Understanding the composition of atmospheric aerosol particles is necessary for identifying their sources and predicting their effect on various atmospheric processes. Although organic compounds typically account for 10 – 70% of the total dry fine particle mass in the atmosphere [*Gray et al., 1986; Middlebrook et al., 1998*], their concentrations, composition and the processes that control their formation and transformation in the atmosphere are not well understood, particularly in relation to the other major fine particle constituents, i.e. sulphate and nitrate compounds. Furthermore, the contributions of the primary and secondary components of particulate organic carbon have long been difficult to quantify. This is because particulate organic matter is part of a complex atmospheric system with hundreds of different compounds, both natural and anthropogenic, covering a wide range of chemical and thermodynamic properties [*Saxena and Hildemann, 1996*]. The presence of semi-volatile compounds complicates the sampling of organic particulate matter (see chapter 2). In addition, there is a current lack of a single technique that is capable of analysing the entire range of organics present. The lack of a direct chemical analysis method for the identification of the composition of organic aerosols and the separation of the primary and secondary sources has led researchers to employ several indirect methods. These include the use of tracer compounds for either the primary or the secondary OC [*Gray et al., 1986; Turpin and Huntzicker, 1991*], the use of models describing the formation of secondary OC [*Pandis et al., 1992*] and the use of models describing the emission and dispersion of primary OC [*Harley and Cass, 1995*].

Over the past decade or so, aerosol mass spectrometry has gained considerable interest as a means of correlating the size and chemical composition of particles in real-time. The Aerodyne aerosol mass spectrometer (AMS) has represented a significant step forward in this area of research. The instrument employs an aerodynamic lens, differential pumping, aerodynamic sizing, thermal vaporisation, electron impact ionisation and quadrupole mass spectrometry, where particles are analysed within a few milliseconds of entering the vacuum. The AMS has been shown to be capable of providing quantitative information on the chemical composition of the submicron non-refractory fraction of aerosol particles with a high size and time resolution [*Jayne et al., 2000; Allan et al., 2003a; Jimenez et al., 2003b; Alfarra et al., 2004; Drewnick et al., 2004a; Drewnick et al., 2004b*]. In this work, the capability of the AMS to measure organic aerosols has been verified and the instrument has been utilised to provide insights into the sources, composition and processes of atmospheric organic aerosols. A review of other techniques to measure the chemical and physical properties of atmospheric aerosols is first presented in chapter 2. The AMS is then described in detail in chapter 3, while laboratory experiments that were performed to characterise its response to organic particles are discussed in chapter 4. AMS measurements of atmospheric aerosols in various locations around the world, representing urban, rural and remote settings have been carried out. Atmospheric processing and the chemical and physical characteristics of the aerosol organic fraction at these locations are described in chapter 5. The formation of secondary organic aerosols (SOA) from the photooxidation of anthropogenic and biogenic precursors has been investigated using a reaction chamber. The chemical signatures of the products and the atmospheric implications of such processes are presented in chapter 6. Finally, the characteristics of cloud and aerosols at a high-alpine location and the impact of the organic fraction on the mass scavenging of the aerosol particles by cloud droplets are discussed in chapter 7.