Chapter 1

Physical and Chemical Properties of Atmospheric Aerosols

Jay Turner and Ian Colbeck

1.1 Introduction

Particles in the atmosphere are distinguished by their size, shape and composition. They can be directly emitted from sources and can be formed in the atmosphere by chemical reactions and physical processes. Once particles are formed, their properties can be modulated in space and time by atmospheric physical and chemical processes, such as condensation, evaporation and coagulation. Eventually, the particles are removed from the atmosphere by wet or dry deposition, with such removal occurring minutes to weeks after their release or formation, and after travelling metres to thousands of kilometres. This chapter summarises key physical and chemical properties of atmospheric aerosols. These properties can be described at various levels of aggregation (bottom-up, from the single-particle perspective) or discretisation (top-down, from the aerosol perspective). An accounting of each particle by size and composition would provide the finest resolution. In contrast, the bulk composition over all particles would be the coarsest resolution. Furthermore, given the dynamic nature of atmospheric aerosols, the degree of time integration is important.

Particles in the atmosphere are directly emitted by sources (primary emissions) or formed in the atmosphere by physicochemical processes (secondary formation) [1]. Combustion and other high-temperature processes are largely responsible for primary emissions of fine-mode particles, while mechanical processes such as grinding, entrainment of dust and soil and droplet formation by waves generate coarse-mode particles. Condensable gases can homogeneously nucleate to form new particles in the atmosphere if there is insufficient surface area for their uptake. Heterogeneous condensation is the uptake of vapour by pre-existing particles, with the reverse process of evaporation also important.

A summary of the atmospheric aerosol properties must necessarily reflect upon the methods used to arrive at the current state of knowledge. As tools to probe the atmosphere continue to advance, refinements will be made to the understanding of atmospheric aerosols. Starting with the dimensions of size, composition, space and time, observational data are collected from measurements that integrate across these dimensions. Most observational data have been collected at fixed locations, although more data are being obtained from satellite and other profiling instruments that provide spatial resolution [2, 3]. The spatial zone represented by monitoring at a fixed site will depend on the property of interest. It may be possible to infer
the zone of representation from temporal patterns in the data, but in most cases the zone of representation is determined by monitoring at several sites over the spatial scale of interest, such as an urban area. This is tractable for relatively simple measurements but is not tractable for more advanced, research measurements.

Time resolution of the measurements also shapes the understanding of dynamical aspects of aerosol properties. Routine networks for particle mass and, more recently, composition typically collect samples over 24-h periods with frequency of every day to once every several days. Continuous monitoring of particle mass concentration is now common with data typically reported as hourly averages [4]. This is very important for real-time health advisory reporting and to bring the particle mass measurements closer to the characteristic timescales for variations in the weather, emission rates and atmospheric processes that drive variations in particle properties.

Routine measurements are integrated across size and composition. Routine networks typically sample particles in one size range (PM$_{2.5}$, PM$_{10}$: particulate matter (PM) below a specified size; e.g. 10 refers to 10 $\mu$m) and report the bulk composition of the collected particles [5]. The composition measurements are incomplete; some compounds are not measured (e.g. water) and some components are characterised by lumped parameters (e.g. carbonaceous matter) rather than a detailed accounting of each compound. Table 1.1 shows the parameters reported for two routine particle composition networks operated in the United States. In Europe specification of ambient PM is mainly focused on determination of the secondary inorganic aerosol constituents, sulphate ($\text{SO}_4^{2-}$), nitrate ($\text{NO}_3^-$) and ammonium ($\text{NH}_4^+$) via EMEP (Co-Operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) stations [6]. The carbonaceous content of the aerosols are measured only at a very few stations, but has been extensively addressed during measurements campaign, such as the EMEP Elemental/Organic Carbon campaign [7].

Averaging takes place not only in data collection but also in data reduction and analysis. Sites in routine networks with 24-h sampling are typically compared as annual or seasonal

### Table 1.1 Example of monitoring networks involving aerosol composition measurements in the US

<table>
<thead>
<tr>
<th>Network</th>
<th>Start year</th>
<th>Number of sites</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Air Status and Trends Network (CASTNet)</td>
<td>1990</td>
<td>87</td>
<td>Sampling schedule: filters exposed over 7 days to produce 7-day averages (Tuesday to Tuesday) Gaseous: SO$_2$, HNO$_3$, O$_3$ Particulate: SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, other relevant ions</td>
</tr>
<tr>
<td>Interagency Monitoring of Protected Visual Environments (IMPROVE)</td>
<td>1987</td>
<td>Over 160</td>
<td>Sampling schedule: 24 h every third day Particulate: element and organic C, SO$<em>4^{2-}$, NO$<em>3^-$, Cl$^-$, elements between Na and Pb PM$</em>{10}$ and PM$</em>{2.5}$ (mass) Selected sites: light scattering and/or extinction coefficient</td>
</tr>
</tbody>
</table>


averages. Data collection at higher time resolution is often expressed as diurnal profiles, including weekend versus weekday differences [8, 9]. Finally, there can be cataloguing of the frequency of certain types of episodes or events.

Capabilities have existed for some time to measure the size of individual particles [10]. Small particles are typically differentiated by their mobility in an electric field, while larger particles are differentiated by differences in their light scattering or aerodynamic behaviour. There are subtle issues involved in each of these measurements, which should be considered when interpreting the data. Instruments that size, count and determine the chemical composition of individual particles have been developed over the past 15 years. Various single-particle spectrometers now exist, which couple a size measurement to a composition measurement [11, 12]. There are limitations to the size ranges, composition measurements and counting statistics, and significant data aggregation is needed to make the analysis and interpretation tractable. However, these approaches do collect a spectrum for each particle and the analyst can decide how to best reduce the data to fit the project needs.

This chapter summarises the key physical and chemical properties of the ambient aerosol. Emphasis is placed on fine PM in urban areas, as viewed from observational data (rather than modelling). It is beyond the scope of this chapter to exhaustively summarise the myriad features that are observed on the various spatial and temporal scales. Instead, examples are used to introduce the key characteristics with the caveat that emissions, atmospheric dynamics, weather and other factors that influence aerosol chemical and physical properties can lead to significant differences between settings.

1.2 Ambient aerosol size distributions

Many physical properties of ambient aerosols can be estimated from their size distribution and chemical properties [13–15]. Examples include light scattering and absorption properties that are important in both visibility and climate change contexts. This section summarises key features of atmospheric aerosol size distributions.

1.2.1 Idealised size distributions of aerosol number and mass

An aerosol in which all particles are of the same size is termed monodisperse. Such an aerosol is rare and those generated in the laboratory for instrument calibration have a spread in particle diameter of a few percent. Typically, aerosols contain a wide range of sizes and are termed polydisperse. Because of the presence of a range of sizes the problem arises of how to describe the size distribution. In the atmosphere particle size is determined by the formation process and subsequent physical and chemical reactions.

In practice, the form of size distributions, although containing the same modes, can look very different according to whether the distribution is plotted as number distribution or mass distribution. The reason for this is that particles at the small end of the size distribution can be very abundant in number, but because mass depends upon the cube of diameter, such particles may contribute only a small amount of the total mass. Hence, a size distribution expressed as the number of particles per size fraction will give far more emphasis to the smaller particles than will occur in a distribution expressed by mass per size fraction.
Figure 1.1 shows the distribution of aerosol mass as a function of particle size for an idealised urban aerosol. There are two modes – a fine mode and a coarse mode – with particles in these modes generally originating from different source types and having different atmospheric fates (to be discussed later in this chapter). The distribution of aerosol mass and other properties between these two modes can vary in both space and time. The fine-mode particle can be further subdivided into nuclei and accumulation modes. Figure 1.2 shows the aerosol volume distribution for an idealised traffic aerosol. Here there are three modes. The smallest one is the nucleation mode whereby particles have recently been emitted from processes involving condensation of hot vapours, or freshly formed within the atmosphere by gas to particle conversion. Such particles account for the preponderance of particles by number, but because of their small size account for little of the total mass of airborne particles. Due to their high number concentration they are subject to rapid coagulation and/or condensation of vapours and they enter the accumulation mode. Here they generally account for most of the aerosol surface area and a substantial part of the aerosol mass. Accumulation-mode particles have a typical atmospheric lifetime of around 1–2 weeks, as removal by precipitation scavenging or dry deposition is inefficient. These particles are therefore involved in long-range transport. The coarse mode relates to particles greater than 2 μm and which are mainly formed by mechanical attrition processes, and hence soil dust, sea spray and many industrial dusts fall within this mode.
Several studies have demonstrated that size distributions of ambient aerosols can be represented by modes. A distinction must be made between aerosol characterisation based on size cuts and modes. For example, aerosol mass typically has a fine mode and a coarse mode with an overlap of these modes in the range of about 1–3 μm in diameter. For regulatory and indeed most research applications, however, size ranges are defined by the sampler characteristics. The extent to which PM$_{2.5}$, which itself is not a perfect size discriminator but rather depends on the sampler, represents fine-mode aerosol depends on the extent to which the coarse-mode particle extends below 2.5 μm in diameter. This is an important distinction that must be considered when describing the aerosol in terms of fine- and coarse-mode properties [17].

An examination of the evolution of PM air-quality standards in the U.S. demonstrates the relationships between commonly reported PM size cuts and the dominant aerosol mass modes. Starting in 1971, the Ambient Air Quality Standard (NAAQS) for PM was based on the mass concentration of total suspended particulate (TSP). In 1987, this indicator was replaced with PM$_{10}$ because TSP levels were often driven by a few very large particles, while health effects generally correlated with smaller particles, indeed those particles in the respirable size range, which is generally characterised by PM$_{10}$. Finally, in the light of health effects data, United States Environmental Protection Agency revised the PM NAAQS in 1997 to include an indicator for the fine mode only – namely, a PM$_{2.5}$ standard. As shown in Figure 1.1, the samplers used to collect a given size fraction do not exhibit a sharp cut at the stated particle size nor do they rigorously represent a specific mode. For example, a PM$_{10}$ sampler will collect a few particles as large as 20 μm and will not collect all particles in the size range 5–10 μm. For this reason, the
PM NAAQS are actually defined as the mass concentration for particles in a given size range as collected by a specific sampler design.

In summary, the following size ranges are defined:

- **TSP**
  - Total suspended particulate matter (up to $\sim 35 \mu m$ in diameter)

- **PM$_{10}$**
  - Particulate matter smaller than 10 $\mu m$ in diameter

- **PM$_{2.5}$**
  - Particulate matter smaller than 2.5 $\mu m$ in diameter

- **Fine PM**
  - Particles smaller than about 1–3 $\mu m$ in diameter; we shall operationally define as PM$_{2.5}$

- **Coarse PM**
  - Particles larger than 1–3 $\mu m$ in diameter; we shall operationally define as PM$_{10}$ minus PM$_{2.5}$ but it is actually the PM$_{10}$ contribution to the coarse PM mode

- **Ultrafine PM**
  - Particles smaller than about 100 nm

- **Nuclei mode**
  - Particles in the range 5–100 nm

- **Accumulation mode**
  - Particles in the range 100 nm–2 $\mu m$

Additional size ranges may be reported with names such as ‘inhalable’ or ‘respirable’.

Figure 1.3 shows typical distributions for aerosol number, surface area and volume as a function of particle size for ambient air. These three curves represent the same aerosol; we are merely considering different properties of this ensemble of particles as a function of particle size. The aerosol number concentration, $N$, is unimodal, with a peak around 0.01 $\mu m$. The aerosol volume concentration per unit volume of air, $V$, is bimodal, with a minimum in the range 1–3 $\mu m$. The idealised aerosol mass distribution of Figure 1.2 at least qualitatively resembles the volume distribution of Figure 1.3, with some differences arising from differences in particle density as a function of size because the composition is also changing as a function of size.

### 1.2.2 Size distribution measurements

The distribution of aerosol properties as function of size has significant implications to behaviour of the ensemble of particles. There are various approaches to characterising such behaviour. For a given property of interest, it might be possible to directly measure that property for size-selected aerosols. Alternatively, if the functional relationship between particle size and the property of interest is known, then a measurement of the number size distribution can be used to determine the ensemble behaviour. For this reason, this section focuses on number size distributions of atmospheric aerosol, although other size distributions (especially mass) are discussed.

Time-integrated sampling has been used to determine aerosol size distributions for a number of properties. In some cases, overlapping size ranges are sampled and the size distribution is determined by difference. For example, PM$_{2.5}$ and PM$_{10}$ mass are measured at numerous sites with the coarse aerosol contribution to PM$_{10}$ determined by difference (i.e. PM$_{10,0–2.5}$). The differencing method can be simple, but the propagated sampling and analytical uncertainties can become quite large in some cases. Another approach is size-selective sampling, where the sampler sorts the particles into size bins. For the example of determining the coarse aerosol contribution to PM$_{10}$, a dichotomous sampler can be used to separate the aerosol into fine particulate matter (PM$_f$) and coarse particulate matter (PM$_c$) bins. A correction must be applied for fine particle intrusion into the coarse particle bin, and typically the rate of change...
of selection with size (the so-called sharpness of the size cut) is broader, which leads to some sampling overlap between the bins. In other cases, the goal is not to split the aerosol into two or more streams for collection but rather to sequentially select out particles from the sample stream. Cascade impactors are used to deposit aerosols of increasing smaller, discrete size ranges onto substrates for subsequent analysis [11]. Various impactor designs are available to meet a variety of measurement objectives, ranging from personal sampling for exposure studies to the collection of large sample volumes for toxicological studies.

Since the particle size of interest in aerosol behaviour ranges from molecular clusters of 0.001 μm to fog droplets and dust particles as large as 100 μm, a variation of $10^5$ in size, one cannot use a single instrument to cover the full range. There is constant effort to improve aerosol instrumentation so that various physical or chemical properties can be determined over a wider size range, to develop new measurement techniques and to increase sensitivity. To characterise the chemical composition of the complex atmosphere, a complementary collection of different analytical methodologies is typically used. Several factors must be taken into consideration when instruments are being developed for these measurements. Ideally, the technique should be fast enough to track changes in concentration, composition, or both as they occur, sensitive enough to detect the species of interest and free of interferences from other species present in the same air mass.
Typically, instrumentation is split into two approaches: direct-reading measurements, and collection and analysis [12]. The former yields virtually instantaneous results and results in many measurements to be made, while the latter is generally less expensive and more time consuming, but provides both qualitative and quantitative measurements.

It is often assumed that the sample of particles collected for analysis is representative of those airborne particles from which the sample was taken. For gases this assumption is reasonable, provided buoyancy (and density) considerations are taken into account during the sampling, and the collected samples are kept under appropriate temperature conditions. However, particles do not behave the same way as gas molecules when dispersed in air; they deposit under gravity, impact on bends due to particle inertia, are deposited on internal surfaces by molecular and turbulent diffusion and are affected by thermal, electrostatic and acoustic forces. In addition, the efficiency with which particles are sampled is governed mainly by inertial and sedimentation forces, with other forces playing a role dependent upon the nature and size of the particles and the sampler, and upon the environmental conditions during which the samples were taken. In situ measurements are the least invasive whereby measurements, generally by optical techniques, are made without moving a sample from a flowing aerosol stream.

The instrument selected for a particular application will depend on several factors. In particular, one needs to know why does one want to sample PM and how the results will be used.

All of the above approaches, regardless of the level of time integration, provide information in discrete size bins. The final representation of the data might be in such bins, either in raw form (the parameter as measured for size-segregated sample) or after processing the data through an ‘inversion algorithm’ to account for the size segregation not being step functions. Another approach is to fit a continuous distribution to the data and report the results as properties of the continuous distribution, such as its ‘moments’. A reconstruction of the size distribution requires knowing the transmission efficiency through the instrument as a function of size, as only a fraction of the particles are actually measured and there is size-selective bias in the penetration of particles into and through the analyser.

Single-particle analysers can be used to continuously measure the particle properties [18–20]. The advantage offered by single-particle mass spectrometers relative to pre-existing means of characterising airborne particles is that the single-particle mass spectrometer is able to generate information individually on the chemical composition of large numbers of particles as a function of their size rather than integrate that information across all of the particles collected over a period of hours, as happens with traditional bulk chemical measurements. It therefore provides direct information on the chemical associations of different elements within individual particles, whilst traditional bulk analysis would require uncertain inferences to be drawn regarding such chemical associations [21].

No attempt is made in this chapter to exhaustively examine the opportunities and challenges in constructing size distributions of atmospheric aerosols. The intent is merely to articulate that the measurement issues should be carefully considered in the interpretation of reported size distributions.

1.2.3 Dynamics of atmospheric aerosol size distributions

The aerosol size distribution measured at any instant will be a complex function of the emissions contributing to the aerosol burden in the air mass, atmospheric processing of the air mass
including the formation of new particles and condensation onto existing particles, and removal processes through evaporation, scavenging and deposition.

Size distributions for primary emissions from sources with discrete emission points (e.g. stacks and tailpipes) are typically characterised by inserting a probe into the emission zone and carefully diluting the exhaust to [22] conditions. This approach provides a framework to collect samples from various sources – within a given source category and across numerous source categories – under a common set of conditions. While a standardised approach has many advantages, it does not necessarily capture the dynamics that occur proximate to the emission point which could substantially influence the size distribution that represents the contribution of this source to ambient burdens. A simplistic viewpoint is one of each emission source releasing particles that rapidly mix with ‘background’ air and simply add to the total particle burden. In many cases, however, the process is much more complex, with plume dynamics occurring downwind of the release point.

For example, Zhang et al. [23–25] developed a conceptual model for the evolution of particle number distributions from motor vehicle exhaust. Plume processing is divided into two stages – a ‘tailpipe-to-roadway’ stage and a ‘roadway-to-ambient’ stage. These stages have distinguishing characteristics that influence the particle size distribution observed at ambient conditions. The tailpipe-to-roadway stage features a steep temperature gradient with mixing driven by vehicle-induced turbulence and dilution on the order of 1000-fold in about 1 s. The roadway-to-ambient stage features relatively constant temperature with mixing driven by atmospheric shear and stability and dilution less than tenfold dilution in 3–10 min. Spatial scales for these two stages are 2–3 and 50–100 m, respectively. Plumes from individual vehicles are relatively isolated during the first stage but become co-mingled during the second stage. In the tailpipe-to-roadway stage, sulphuric-acid-induced nucleation provides fresh aerosol that rapidly grows by organic vapour condensation. In the tailpipe-to-roadway stage, particles can continue to grow by condensation but might also evaporate depending on the partial pressures on condensed organics in the diluted gas phase. The net effect is large numbers of particles smaller than 6 nm being emitted from the roadway, with these particles growing to above 10 nm within the first 30–90 m downwind. Thereafter, some of these particles will continue to grow into the accumulation mode, while others will shrink. Figure 1.4 shows measurements by Zhu et al. [26] that were simulated by Zhang et al. [24], using a sectional aerosol model to elucidate the governing dynamics. There are dramatic changes to the particle size distribution over the first 300 m downwind of the roadway. These dynamics have important implications to understanding exposures at dwellings proximate to roadways and also the particle size distributions used to represent motor vehicle emissions in Eulerian transport models where the finest resolution for temporal allocation of mobile source emissions is often the modelling grid cell (typically 4 × 4 km or larger). Similar issues are encountered with other emission sources such as point-source plumes (e.g. combustors) and even re-entrained dust. In the latter case, the size distribution used for Eulerian transport modelling and certain other applications needs to take into consideration near-field losses by deposition.

Atmospheric dynamics can modulate the ambient size distribution. Transformations occurring during transport can have profound effects on size distributions. Homogeneous nucleation events generate large number concentrations of ultrafine particles that can grow by vapour condensation or coagulation. Particles can evaporate, and they can be removed by wet and dry processes. The dynamics of size distributions are typically reported from a Eulerian perspective; the measurement location is fixed and the air parcels are probed as they advect past the site.
Since real-time monitoring is relatively expensive and one of the main reasons for monitoring is to aid in the assessment of human exposure to pollution, numerous papers have been published on methodology to identify ideal sites for pollution monitoring. A full understanding of the complex interactions behind the aerosol environmental effects requires a multidisciplinary approach, involving both experimental and theoretical methods [27–30].

Modern instrumentation allows quantitative measurements of aerosol formation and growth rates. An example of this is shown in Figure 1.5, where size distribution data over the range 3–680 nm have been collected at 5-min resolution, using a scanning mobility particle spectrometer. The measurements were carried out between July 2001 and June 2002 as part of the Pittsburgh Air Quality Study [31]. Analysis of the data indicates that nucleation occurred on 50% of the study days and regional-scale formation of ultrafine particles on 30% of the days. Figure 1.5 depicts the size distributions measured during 10 August and 11 August 2001. The evolution of the size distributions is shown in Figures 1.5a–1.5b, while Figure 1.5c indicates the integrated particle concentration. It is evident that on 10 August 2001 there was no detectable nucleation activity, while an intense nucleation event was observed around 9 am EST on 11 August, followed by rapid growth of the particles to a size around 100 nm [31]. Kulmala et al. [32] have reviewed recent observations of particle formation and growth. The measurements span a broad range of both geographical locations and ambient conditions. They conclude that
the formation rate of 3-nm particles is often in the range $0.01 - 10 \text{ cm}^{-3} \text{ s}^{-1}$ in the boundary layer. However, in urban areas formation rates are often higher than this (up to $100 \text{ cm}^{-3} \text{ s}^{-1}$), and rates as high as $10^4 - 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ have been observed in coastal areas and industrial plumes.

Removal processes such as wet and dry deposition also alter the aerosol size distribution. For example, Freiman et al. [33] measured particle size distributions at five sites in Haifa, Israel, including two pairs of sites that were closely matched in the characteristics that govern variability in particle matter properties over short spatial scales [34, 35]. Mass size distributions were measured over the range $0.23 - 10 \mu m$ and differences were observed between the paired sites. For all size ranges, the less vegetated sites exhibited higher mass concentrations than the more vegetated sites and these differences could not be explained by factors such as meteorology or local emissions. It was concluded that vegetative cover was responsible for differential removal rates of particles between the sites, leading to differences in the aerosol mass–size distributions.

### 1.2.4 Features of selected ambient aerosol size distributions

In light of the above factors, it is evident that aerosol size distributions can vary in space in time due to differences in emission sources and atmospheric processes. The construct of a ‘representative’ size distribution (e.g. temporally averaged for a fixed site) necessarily smoothes
out many of the features that may be of interest but nonetheless has value. Jaenicke [36, 37] presented idealised number and volume distributions for several classes of tropospheric aerosols (Figure 1.6). The key features of each class are as follows:

- **Polar aerosols** are present near the ground in the Arctic and Antarctica. Number concentrations are very low with significant contributions from aged, globally transported aerosols.
- **Background aerosols** are measured in the free troposphere (FT) above the clouds, operationally above 5 km. When measured in remote regions they can represent conditions over large spatial domains, such as continents.
- **Maritime aerosols** are present over the oceans. They are a mixture of background aerosols and sea salt. The sea salt is predominantly coarse aerosol (by mass).
Remote continental aerosols are measured at the surface at locations with small influences by humans. Desert dust storm aerosols originate from locations such as the Gobi and Saharan deserts. They can be transported around the globe. Rural aerosols are continental aerosols at sites with some degree of anthropogenic impacts. Urban aerosols are measured at the surface in population centres and are influenced by a variety of anthropogenic activities. Biological aerosols are particles derived from living organisms. They can be viable (alive) or non-viable (dead) in the atmosphere and include materials such as pollens, spores, bacteria and plant fragments.

As Figure 1.6 demonstrates, there are dramatic differences in these aerosol size distributions. For instance, polar aerosols reflect their aged nature as well as their low concentrations. For the urban environment, the maximum particle concentration is observed for small particle sizes and drops off significantly towards minimum values of just a few particles per cubic centimetre for particles in the 10-μm range. Urban aerosols are a mixture of primary particulate emissions from industries, transportation, power plants and natural sources. Secondary material from gas-to-particle conversion also contributes to the urban aerosols. Generally, the size distribution of urban aerosols is very variable. High concentrations of small particles are found near sources, and fall off rapidly with distance from these sources [1]. Desert aerosols exhibit the greatest concentration of coarse particles of any of the classes. In fact, aerosols resuspended from the world’s deserts can be transported over considerable distances. Such particles contain essential minerals and can play a major role in fertilising nutrient-limited regions. Annual global dust emissions range from 1000 to 3000 Tg per year [38]. In Figure 1.6b it is clear that the mode diameter increases when going from a number through to a volume distribution, again emphasising the way in which submicron aerosols dominate the number distribution and supermicron aerosols the volume distribution.

Over the past 15 years there has been a dramatic increase in measurements of atmospheric aerosols in various settings. For example, long-term measurements have been conducted at the Jungfraujoch (JFJ) High Alpine Research Station in Switzerland. This site is predominantly in the free troposphere (FT) but is periodically in the planetary boundary layer (PBL), and is presumed representative of the continental aerosol over remote regions of Europe. Figure 1.7 shows seasonal average FT size distributions for the JFJ site compared to the polar, background and remote continental model distributions [13]. The JFJ measurements more closely resemble the model remote continental distribution than the model background distribution.

Desert dust storm aerosols are characterised by high concentrations of coarse particles. The sizes distributions will be attenuated during transport due to preferential removal of the largest particles by sedimentation. Figure 1.8 shows aerosol number distributions measured in Seoul, Korea [39], during April 1998. The baseline number distribution for this urban setting is high (open circles) but excursions were nonetheless observed during periods with moderate (closed circles) and heavy (closed triangles) dust periods from dust storms over the Gobi Desert in Western China and Mongolia.

Biological aerosol particles can be a significant component of the ambient aerosol. Figure 1.9 shows primary biological aerosol particle size distributions measured at a site with both urban and rural influences (Mainz, Germany), a remote continental site (Lake Baikal, Russia) and a marine site (on the Atlantic Ocean). Particle number concentrations ranged from 0.6 cm$^{-3}$ at
Figure 1.7 Seasonal average number size distributions measured for the free troposphere at Jungfraujoch, Switzerland, and model size distributions from remote continental, polar and background aerosol classes. (Reproduced from [13] by permission of American Geophysical Union. Copyright 1998 American Geophysical Union.)

the marine and remote continental sites to 3 cm$^{-3}$ at the urban/rural site and, owing to the relatively large particle sizes, they account for a significant fraction of the total aerosol volume at all three locations [40–42].

Size distributions for urban aerosols have been measured in various settings around the globe [43–58]. Figure 1.10 shows mean size distributions for three sites in and around Houston, Texas, between June and October 2001 [59]. Mean PM$_{2.5}$ mass concentrations were 13.34 µg m$^{-3}$ at HRM-3 (east Houston, industrial source region), 12.25 µg m$^{-3}$ at Aldine (north-central Houston, urban receptor site) and 9.66 µg m$^{-3}$ at Deer Park (east Houston, industrial/residential source region). The size distributions suggest that there are significant primary aerosols released near the HRM-3 site; these primary-mode (<0.1 µm diameter) particles have generally coagulated into larger particles by the time they reach Aldine. Analysis of the size distributions as a function of time of day indicates that the HRM-3 site remains dominated by the primary-mode particles throughout the day, while the Aldine site and the Deer Park site show a much stronger diurnal pattern, with morning and afternoon peaks in number concentrations of particles [59].

An example of the daily variation in the total particle number and mass concentration in developing countries is shown in Figure 1.11 [60]. For New Delhi mean PM$_{10}$ concentration during the measurements was 360 µg m$^{-3}$, which is at the high end of the PM$_{10}$ concentrations reported in other developing countries (Table 1.2). The long-term average PM$_{10}$ levels in urban air over Europe and Northern America are much lower, being typically in the range 10–40 µg m$^{-3}$ and practically always <100 µg m$^{-3}$ [68–70]. The average total particle number
concentration (3–800 nm) during our measurement period was 63 000 cm$^{-3}$, which is two to five times higher than the annual average particle number concentrations measured in various urban sites in Europe and the United States [55, 56, 71]. For Beijing, concentrations were just below those for New Delhi.

1.3 Major chemical components of ambient fine particulate matter

The composition of atmospheric aerosols is seldom simple, with their composition being determined by the sources of primary particles and for secondary particles by the processes forming the particles. Coarse particles ($\geq 2.5$ μm) are generally formed by mechanical processes
such as fragmentation and are rich in Ca, Fe, Si and other naturally occurring earth constituents, as well as sea salt, NaCl. Fine particles (<2.5 μm) are usually formed by combustion or gas-to-particle conversions and can be rich in C, sulphates, ammonium and nitrate ions, as well as trace toxic species (As, Cd, Cs, Sr, Zn and Se).

The concentration, composition and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. Particles from specific sources can fall into characteristic size ranges and, therefore, particle composition can vary with particle size, reflecting this effect. For example, sulphate arising from the oxidation of SO₂ is typically present in fine particles, whereas silicon from the resuspension of soils and surface dusts is normally found in coarse particles. The composition of the individual particles can be fairly uniform (internally
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Figure 1.10  Mean size distributions for particulate matter at HRM-3 (east Houston, industrial source region), Aldine (north-central Houston, urban receptor site) and Deer Park 2 (east Houston, industrial/residential source region). Mean distributions are over several measurements taken during July to October 2001. (Reproduced from [59] with permission. Copyright 2004. American Association for Aerosol Research, Mount Laurel, NJ.)

Figure 1.11  (a) Four-hour averages of number (3–800 nm) and mass concentrations (<10 μm) between 26 October and 2 November in New Delhi, India. Left axes are for number concentration (dashed line) and right axes for mass concentration (solid line). (b) Four-hour averages of total number (3–800 nm) and mass concentration (<10 μm) in Beijing, China, from 26–31 July 2004 (Monday to Saturday). (Reproduced from [60] with permission from Springer Science and Business Media.)
<table>
<thead>
<tr>
<th>Country</th>
<th>City</th>
<th>Environment type</th>
<th>Population</th>
<th>Representativeness</th>
<th>Season/monsoon season</th>
<th>TSP</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>India</td>
<td>Mumbai</td>
<td>Residential</td>
<td>10 million</td>
<td>Few days, 1996 [61]</td>
<td>Winter</td>
<td>197</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Slum</td>
<td></td>
<td>Few days, 1996</td>
<td>Winter</td>
<td>127</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Coastal urban</td>
<td></td>
<td>1 month, 1999 [62]</td>
<td>Winter</td>
<td>182</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1 month, 1999</td>
<td>Winter</td>
<td>128</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>New Delhi</td>
<td>Urban</td>
<td>14 million</td>
<td>1 week, 2002 [60]</td>
<td>Autumn</td>
<td>360</td>
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<tr>
<td>China</td>
<td>Beijing</td>
<td>Urban</td>
<td>11 million</td>
<td>1 year, 1999–2000</td>
<td>All</td>
<td>335</td>
<td>176</td>
<td>97</td>
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<tr>
<td></td>
<td>Beijing</td>
<td>Residential</td>
<td></td>
<td></td>
<td>All</td>
<td>350</td>
<td>185</td>
<td>102</td>
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<tr>
<td></td>
<td>Xian</td>
<td>Urban</td>
<td>3.66 million</td>
<td>1 year, 1996–1997</td>
<td>All</td>
<td>410</td>
<td>260</td>
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<td></td>
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<td></td>
<td>Autumn</td>
<td>350</td>
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<td></td>
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<td>1000</td>
<td>640</td>
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<td>Spring</td>
<td>380</td>
<td>243</td>
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<td></td>
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<td>Summer</td>
<td>190</td>
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<td>Bangladesh</td>
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<td>Urban</td>
<td>8.6 million</td>
<td>1.5 years</td>
<td>Low rain</td>
<td>227</td>
<td>88</td>
<td>40</td>
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<td></td>
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<td></td>
<td>Medium rain</td>
<td>85</td>
<td>34</td>
<td></td>
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<td></td>
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<td>High rain</td>
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<td>All</td>
<td>123</td>
<td>51</td>
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<td>40 km from</td>
<td>Rural</td>
<td>8.6 million</td>
<td>1 year</td>
<td>Low rain</td>
<td>98</td>
<td>35</td>
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<td>Medium rain</td>
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<td>High rain</td>
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<td>Pakistan</td>
<td>Karachi</td>
<td>Urban</td>
<td>14 million</td>
<td>1 month [65]</td>
<td>Winter</td>
<td>660</td>
<td>420</td>
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<tr>
<td>Mexico</td>
<td>Ciudad de</td>
<td>Urban</td>
<td>20 million</td>
<td>1 month, 1997 [66]</td>
<td>Winter</td>
<td>80</td>
<td>40</td>
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<tr>
<td>Botswana</td>
<td>Serowe</td>
<td>Village</td>
<td>55 000</td>
<td>2 months, 1999 [67]</td>
<td>Winter</td>
<td>29</td>
<td>10</td>
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mixed aerosols) or very different from the ensemble composition (externally mixed aerosols), depending on the particle sources and atmospheric aging processes involved.

In general, the predominant chemical components of PM are sulphate, nitrate, ammonium, sea salt, mineral dust, organic compounds and black or elemental carbon, each of which typically contributes about 10–30% of the overall mass load. The predominance of these chemical components in PM$_{10}$ and PM$_{2.5}$ and their size distribution are closely linked to the emitting source and the formation mechanisms of the particles.

- **Sulphate** – arises primarily as a secondary component from atmospheric oxidation of SO$_2$;
- **Nitrate** – typically present as NH$_4$NO$_3$, resulting from the neutralisation of HNO$_3$ vapour by NH$_3$, or as sodium nitrate (NaNO$_3$), due to displacement of hydrogen chloride from NaCl by HNO$_3$ vapour;
- **Ammonium** – usually present in the form of ammonium sulphate ((NH$_4$)$_2$SO$_4$) or NH$_4$NO$_3$;
- **Sodium and chloride** – from sea salt;
- **Elemental carbon** – formed during the high-temperature combustion of fossil and biomass fuels;
- **Organic carbon** – carbon in the form of organic compounds, could be either primary, resulting from automotive or industrial sources, or secondary, resulting from the oxidation of volatile organic compounds;
- **Mineral components** – mainly present in the coarse fraction and rich in elements such as aluminium, silicon, iron and calcium;
- **Water** may also be present within, for example (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, and NaCl. The water-soluble components can take up water from the atmosphere at high relative humidity, thereby turning from crystalline solids into liquid droplets.

In addition to the above there are many minor chemical components present in airborne particles. Their detection is often a function of the sensitivity of the analytical procedure. Such components include the following:

- **Trace metals** – such as lead, cadmium, mercury, nickel, chromium and zinc;
- **Trace organic compounds** – although the total mass of organic compounds can comprise a significant part of the overall mass of particles, it is made up of a very large number of individual organic compounds, each of which is present at a very low concentration.

At different locations, times, meteorological conditions and particle size fractions, however, the relative abundance of different chemical components can vary by an order of magnitude or more [1, 72–74]. Figure 1.12 illustrates how particle number concentration, size distribution and chemical composition of fine particulate vary in urban and high Alpine air. The dotted lines indicate characteristic particle size modes, which can be attributed to different sources, sinks and aging processes of atmospheric particles: nucleation (Aitken), accumulation and coarse modes.

In the UK intensive research on the chemical characterisation of PM$_{10}$ has been summarised by Air Quality Expert Group [4]. Data for four roadside sites and four urban background sites have been investigated and show that [75]:

- The marine contribution is estimated at around 2 μg m$^{-3}$ in PM$_{10}$ (8 and 6% in urban background and roadside sites) and only 0.3 μg m$^{-3}$ in the PM$_{2.5}$ fraction (1–2% of PM$_{2.5}$
mass). These values are very similar to those reported for Berlin and Spain, and lower than the Dutch levels.

- Road dust levels reach 5.5 and 6.5 μg m⁻³ in PM₁₀ (22 and 18% at urban background and roadside sites) and only 1.6 μg m⁻³ in the PM₂.₅ fraction (11% of PM₂.₅ mass). These values are relatively low when compared with data obtained from Spain, and similar to the data reported for the Netherlands.
- The levels of carbonaceous components reach 9.3 and 18.1 μg m⁻³ in PM₁₀ (38 and 50% at urban background and roadside sites). These values are in the range of data reported for Berlin and Spain, and higher than the values reported for the Netherlands.
- Organic carbon (OC) predominates over elemental carbon (EC) at urban background sites (26% versus 12% in PM₁₀), whereas in roadside sites similar levels are determined for both type of carbonaceous in PM₁₀.
- The carbonaceous components are mostly present in PM₂.₅. Thus, around 90 and 80% of the OC and EC mass, respectively, are present in fine fractions at both background and roadside sites. Around 50 and 65% of the PM₂.₅ mass at urban background and roadside sites is made up by carbonaceous compounds.
- Levels of secondary inorganic are close to 8 μg m⁻³ in both urban background and roadside sites, accounting for 32 and 23% of the PM₁₀ mass, respectively, in the range of levels found for the other European Union examples reported here.
The ratio ammonium sulphate/ammonium nitrate in PM$_{10}$ is also constantly 1:1 at both type of sites, and around 30% of nitrate in PM$_{10}$ is present in the coarse mode ($PM_{2.5-10.0}$, probably as sodium nitrate), whereas this proportion is around 12% in the case of ammonium sulphate.

### 1.4 Aerosol composition as a function of size

Preceding sections focused on particle size distributions without regard to particle composition, and particle composition for fine and coarse PM without further size discrimination. In this section, we draw attention to joint size–composition distributions that can be particularly valuable in understanding the physical and chemical mechanisms that govern ambient aerosols. In the preceding section it is evident that specific compounds will occur in certain size ranges. Crustal minerals such as calcium, magnesium, aluminium and iron are typically found in the coarse fractions, whereas sulphate, ammonium, organic and elemental carbon and certain transition metals occur mainly in the fine fractions.

Herner et al. [76] examined size–composition distributions collected for winter conditions at five sites in (or near) the San Joaquin Valley of California as part of the California Regional Particulate Air Quality Study. Distributions for a coastal site were stratified into periods with onshore versus offshore winds, while distributions for inland sites were stratified into daytime versus nighttime periods. Examples of these average distributions are shown in Figure 1.13.
PM$_{10}$ mass at the coastal site is dominated by coarse PM sea salt during periods with onshore winds (Figure 1.13a). Offshore winds coincide with much lower PM$_{10}$ mass concentrations with more fine mass than coarse mass and a peak at 0.5–1.0 μm which is primarily ammonium nitrate (Figure 1.13b). Average daytime aerosol in Sacramento (Figure 1.13c), a large inland city, has a distribution qualitatively similar to the coastal offshore distribution with the most excess mass at the coastal site being coarse PM. The average Sacramento nighttime distribution (Figure 1.13d) is dramatically different; it is dominated by carbonaceous aerosol arising from primary emissions. The size–composition distributions were simulated using a box model to determine the relative roles of condensation/evaporation, hygroscopic growth, dry deposition, emissions and coagulation to arrive at a detailed conceptual model for ambient PM in the San Joaquin Valley.

An example of the size distribution for the various inorganic compounds is shown in Figure 1.14. Here the size distribution is presented for one urban and two rural sites in British Columbia, Canada [77]. The dominant inorganic chemical component shows a bimodal size distribution at all three sites, with the accumulation mode dominating the mass relative to the coarse-mode peak. SO$_4^{2-}$ dominates the accumulation mode at all sites, with a median peak concentration at 0.3–0.55 μm. NO$_3^-$ shows a prominent coarse mode at >1 μm that resembles that of Na$^+$, but also exhibits a secondary accumulation mode between 0.3 and 1.0 μm. It can be seen that sea salt aerosols, as represented by Na$^+$, are confined to the coarse mode and peak between 1 and 18 μm, depending on location and time. The chloride ion has a similar coarse-mode distribution [77].

Figure 1.15 summarises the size distributions of trace elements collected in the centre of Athens during the summer of 2001 [78]. It is evident that metallic elements in the Athens urban aerosol can be classified into two groups. The first group comprises Cd, V, Ni, Pb and Mn emitted from anthropogenic sources. The second group consists of Al, Fe, Cu and Cr, and is mostly present in the coarse fraction and has its origin in soil dust or mechanical abrasion processes. The second group holds by far the bulk of the aerosol elemental metal mass concentration [78].

1.5 Summary and conclusions

We often assume that air pollution is a modern phenomenon, and that it has become worse in recent times. However, since the dawn of history, mankind has been burning biological and fossil fuel to produce heat. The walls of caves, inhabited millennia ago, are covered with layers of soot and many of the lungs of mummified bodies from Palaeolithic times have a black tone [15, 79]. However, it is only relatively recently that it has become increasingly clear that aerosol particles are of major importance for atmospheric chemistry and physics, the hydrological cycle, climate and human health.

An important aspect in the study of PM is its complexity of the physicochemical characteristics, the multiple sources, morphology and its dynamics that is correlated with the size of the particles.

Atmospheric aerosols originate either from naturally occurring processes or from anthropogenic activity. Major natural aerosol sources include volcanic emissions, sea spray and mineral dust emissions, while anthropogenic sources include emissions from industry and combustion processes. Within both categories further distinction of so-called primary and secondary
Figure 1.14  Box and whisker plots of ionic particle size distributions at the three sites. The dotted line and solid bar in each box represent the mean and median, respectively; the upper and lower parts of each box represent the 75th and 25th percentiles and the extensions represent the 90th and 10th percentiles; any points outside these limits are shown as large filled circles. (Reproduced from [77] with permission. Copyright Elsevier 2006.)
Figure 1.15  Mean size distribution of nine metals (Cd, Pb, V, Ni, Cr, Mn, Cu, Fe and Al). Values are geometric means calculated from 16 samples. (Reproduced from [78] with permission. Copyright Elsevier 2007.)
sources may be made. The direct emission of aerosols into the atmosphere constitute primary sources, while secondary sources arise from the gas-to-particle conversion of gaseous precursor compounds, such as nitric oxide and nitrogen dioxide, sulphur dioxide and hydrocarbons. Particles in the accumulation range arise typically from the condensation of low-volatility vapours and from coagulation of smaller particles in the nucleation mode with themselves or with the larger accumulation-mode particles. Particles tend to accumulate in this mode, as there is a minimum efficiency in sink processes.

Particles in the coarse mode are usually produced by weathering and wind-erosion processes. Chemically, their composition reflects their sources and hence inorganic compounds such as mineral dust and sea salt are found in addition to organic compounds such as biological and biogenic particles resulting from direct emission of hydrocarbons into the atmosphere.

Recent scientific advances now offer an improved understanding of the mechanisms and factors controlling the chemistry of atmospheric aerosols.

References


