Chapter 2

What is particulate matter?

Key points

- Airborne PM includes a wide range of particle sizes and many different chemical constituents. It contains both primary components, which are emitted directly into the atmosphere, and secondary components, which are formed within the atmosphere as a result of chemical reactions.
- Conceptually, airborne particles are usually considered as belonging to three size modes. The smallest is the nucleation mode, which includes particles newly formed through source condensation processes or through atmospheric chemical reactions. These particles grow – through coagulation and vapour condensation – into the accumulation mode, where they may have a long atmospheric lifetime. Particles with a diameter greater than ~1 μm, are referred to as the coarse mode; they are typically generated through mechanical processes such as quarrying or sea spray formation by breaking waves.
- Airborne particles can range in size from a few nanometres (nm) to around 100 μm in diameter. By far the greatest number of particles falls into the ultrafine size range, which is less than 100 nm, whereas the larger particles – although contributing rather little to particle number – contribute the major proportion of particle mass.
- Some constituents of airborne particles, most notably ammonium nitrate (NH_4NO_3) and PAHs are termed semi-volatile and are able to partition between particles and the vapour phase.
- Major chemical components of airborne particles include sulphates, nitrates, ammonium, sodium chloride (NaCl), elemental and organic carbon, mineral particles and coarse, iron-rich particles generated by vehicles.
- Particles in the atmosphere contain chemically bound water that is not removed completely under the drying conditions used in the standard European weighing procedures.

2.1 Introduction

33. Airborne PM presents a far greater complexity than most other common air pollutants. Not only is it a mixture of different chemical substances, but individual particles also span a wide range of sizes. Both chemical composition and size can provide valuable insights into the sources of airborne particles, and these parameters also determine the atmospheric behaviour and fate of particles as well as influencing human health effects. Because these issues have been examined in detail in reports by the Quality of Urban Air Review Group (QUARG, 1996) and the Airborne Particles Expert Group (APEG, 1999), they will be discussed only briefly here.

34. The most important distinction is between primary and secondary atmospheric particles. Primary particles are those emitted directly from a source and therefore include particles that arise directly from combustion sources, such as road vehicles and power stations, as well as those generated by mechanical processes, for example, quarrying and agricultural harvesting. The land and the sea are both major sources of primary particles, through entrainment of soils by the wind and the generation of marine aerosol particles by the bursting of air bubbles entrained in breaking waves. Secondary particles are not emitted directly from sources, either natural or anthropogenic. Rather, they are formed in the atmosphere as a result of chemical reactions that lead to the formation of substances of low volatility, which consequently condense into the solid or liquid phase, thereby becoming PM. Such particles generally result from atmospheric oxidation processes and the substances oxidised may be either natural or anthropogenic in origin.

Box 2.1 Definitions of PM

The following definitions of particle size categories are widely accepted.

- Nanoparticles: particles smaller than 50 nm in diameter.
- Ultrafine particles: particles smaller than 100 nm in diameter.
- Fine particles: particles in the fine mode (see Figure 2.1) or those in the $PM_{2.5}$ fraction. The two may differ.
- Coarse particles: fraction of the measured particle mass concentration determined from PM_{10} minus $PM_{2.5}$.
- $PM_{2.5}$: airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 2.5 μm aerodynamic diameter and which transmits particles of below this size.
- $PM_{2.5–10}$: known as PM_{coarse}.
- PM_{10}: airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter and which transmits particles of below this size.

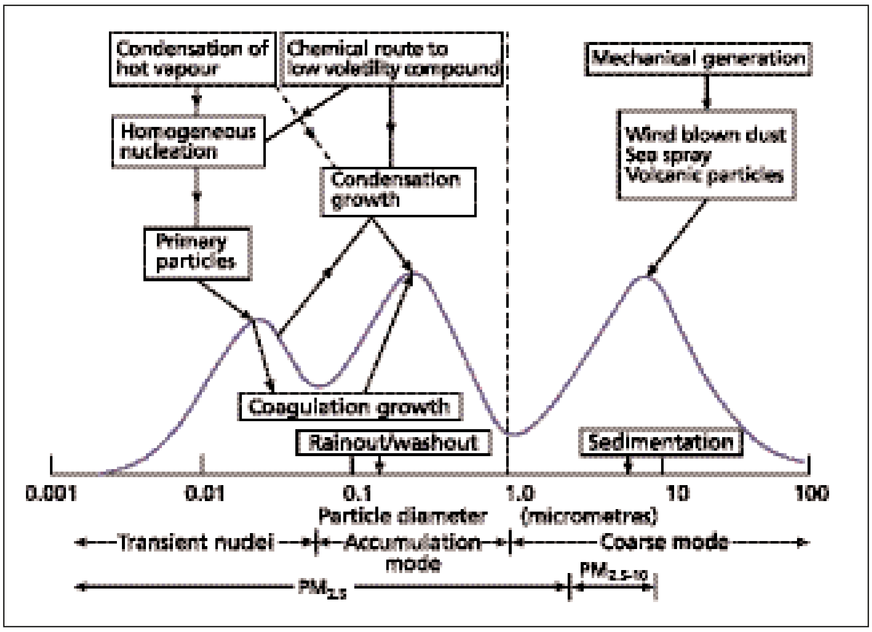
35. The process by which secondary particles are formed is termed nucleation; this term refers to the processes by which molecules of low volatility condense to form solid or liquid matter. There are two distinct types of nucleation process (Hinds, 1999). The first is heterogeneous nucleation. Most secondary particle formation in the atmosphere occurs by this process, newly formed substances condense onto existing particles causing the growth of those particles. The condensation processes are most effective on small and medium sized particles, causing these to grow larger. The second process is called homogeneous nucleation. Some newly formed molecules have extremely low vapour pressure and, in the absence of an abundance of pre-existing particles, will condense with one another to form wholly new particles. The best known process of homogeneous nucleation occurs when sulphuric acid (H_2SO_4) is formed from the atmospheric oxidation of SO_2. This H_2SO_4 can nucleate with water vapour (binary nucleation) or, more readily, with water vapour and ammonia (ternary nucleation) to form droplets of sulphate solution. Measurements made in relatively clean air situations, both over coastlines and the mainland, demonstrate that new particles are frequently formed by condensation of the atmospheric oxidation products of both halocarbons generated from exposed seaweed and hydrocarbons released from forests. In neither case, however, is it wholly clear whether particle formation results from homogeneous nucleation of the oxidation product itself or whether condensation occurs on a primary nucleus formed from H_2SO_4 nucleation.

36. From an air pollution perspective, the secondary components that are of the greatest importance are sulphate arising from the oxidation of SO_2, nitrate from the oxidation of NOx, ammonium from the acid neutralisation of NH_3 gas and secondary organic compounds formed from the atmospheric oxidation of VOCs, largely hydrocarbons.

2.2 Key physical characteristics of airborne particles

37. The behaviour of particles in the atmosphere and within the human respiratory system is determined largely, but not wholly, by their physical properties, which have a strong dependence upon particle size. Figure 2.1 shows, in schematic form, the typical size distribution of airborne particles. Sizes range over several orders of magnitude. The smallest, freshly nucleated, particles are only 1–2 nm in diameter and contain only tens of molecules. At the other extreme, particles may be up to ~100 µm in diameter, which is comparable to a human hair. Particles as large as this rapidly settle out of the air and are of minor health significance because, although they can be inhaled, they do not generally penetrate beyond the nose and mouth. Consequently, air pollution research generally focuses on particles ≤10 µm in diameter, although it is important to recognise that larger particles are also present and contribute mass to 'total suspended' particles (TSP).

Figure 2.1 Schematic diagram of the size distribution of airborne particles.



38. Figure 2.1 divides particles conceptually into three subgroups. These arise in different ways and have quite distinct atmospheric behaviour; they are 'therefore' referred to as separate modes of the distribution.

2.2.1 Nucleation mode

39. The smallest group of particles, with diametres of ≤50 nm, are usually referred to as the nucleation mode; however, some describe the smallest particles, of 10 nm and below, as the nucleation mode and the particles falling between10–50 nm as the Aitken mode. Such particles will have been newly formed either by homogeneous nucleation in the atmosphere (see on previous page) or by nucleation processes that occur within the emissions from high temperature sources and lead to the emission of primary nucleation mode particles. Particles within the nucleation category soon become part of the Aitken category by condensational growth. Such particles have a relatively transient existence in the atmosphere since they readily transform into larger particles and also deposit quite efficiently to surfaces because of their highly diffusive nature, which results from their low individual mass and high tendency to Brownian motion.

2.2.2 Accumulation mode

40. Growth of nucleation mode particles, primarily by vapour condensation but also as a result of coagulation processes, leads to formation of the accumulation mode of particles that are typically between 50 nm and 1 µm in size. Such particles are too large to be subject to rapid Brownian motion and too small to settle from the air rapidly under gravity. Their further growth is inhibited because they do not coagulate as rapidly as fine and coarse particles do and there are diffusion barriers to their growth by condensation. Particles in the nucleation mode can, therefore, have a long atmospheric lifetime, typically 7–30 days, although they are subject to removal by incorporation into rain and this can significantly shorten their atmospheric lifetime.

2.2.3 Coarse particle mode

41. Particles greater than ~1 µm in diameter are typically generated mechanically rather than through the nucleation and condensation processes. Thus, dusts from industrial operations such as quarrying mainly fall into the coarse particle mode as do wind-blown soil and also sea spray. Within this size range, gravitational settling velocities become appreciable and therefore atmospheric lifetimes – although significant – are much shorter than for the accumulation mode particles.

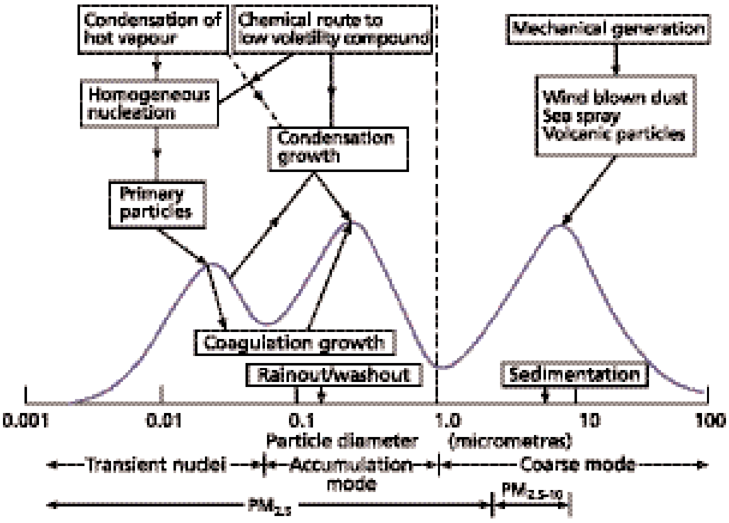
42. It is worth noting at this point that the minimum in particle abundance between the accumulation and coarse particle modes is at ~1 µm and not at 2.5 µm, the size fraction typically used to distinguish coarse and fine fractions during routine air sampling. Thus, typically, a significant proportion of mechanically generated dusts can be sampled within $PM_{2.5}$. One example is Saharan dust, which after long-range transport is substantially within the $PM_{2.5}$ fraction.

43. Coagulation, the process by which particles collide and coalesce together, can be important in aerosol dynamics. This process, which is rapid only when particle number concentrations are high, leads to a general increase in the size of particles. It is, therefore, an important process in the transfer of nucleation mode particles into the accumulation mode. In the absence of fresh emission or new particle formation through nucleation, coagulation processes lead to a gradual reduction in the number of particles and an increase in the mean size.

2.2.4 Number, surface area and volume size distributions

44. While Figure 2.1 shows typical particle size distribution in a schematic form, in practice, the form of size distribution is highly dependent upon whether it is expressed in terms of particle number, surface area or volume/mass. In a typical sample of airborne particles, the vast majority, numerically, are very small in size: it is usual for 70–80% of the number count of particles to be in the ultrafine size range (<100 nm in diameter). However, such small particles have a relatively small surface area and a tiny mass compared to larger particles; therefore, if the distribution of surface area or mass according to particle size is plotted, it looks quite different from the distribution of particle number with particle size. This is exemplified by Figure 2.2, which is taken from measurements of particle number size distributions in suburban Birmingham; these data were then transformed into surface area and volume distributions, assuming spherical particle geometry.

Figure 2.2 Particle size distribution measured in Birmingham.



45. Provided there are no major changes in particle density with particle size, the size distribution of particle mass is very similar to that of volume. Table 2.1 shows the effect of dividing up a single 10 µm particle into particles of 1, 0.1 and 0.01 µm on relative number and relative surface area. Thus, it takes one billion 0.01 µm particles to equal the volume and mass of one 10 µm particle. That one billion 0.01 µm particles has a surface area one million times larger than the 10 µm particle of the same overall volume. Thus, in Figure 2.2, the number size distribution gives great emphasis to the nucleation mode, with the accumulation mode visible. The surface area distribution gives greatest emphasis to the accumulation mode with rather little surface area being associated with nucleation and coarse mode particles. On the other hand, the volume distribution in this case shows two approximately equal modes with a minimum that is close to 1 µm. The nucleation mode contributes insignificantly to particle volume in this example.

Table 2.1 Influence of particle size on particle number and surface area for a given particle mass, assuming spherical geometry.

Particle diameter (µm)	Relative number of particles	Relative surface area
10	1	10
1	10^3	1^2
0.1	10^6	1^4
0.01	10^9	1^6

2.2.5 Semi-volatile components

46. As indicated above, condensation of materials of low volatility is a significant growth mechanism for airborne particles. However, some of the condensable materials themselves have significant vapour pressures and will tend to equilibrate between the particle and vapour phases. An example of substances that undergo such equilibration are the PAHs, which exhibit a wide range of vapour pressures and, therefore, show a range of behaviours, with the two- and three-ringed compounds (for example, naphthalene and anthracene) existing predominantly in the vapour phase (see Table 2.2) and the five-ringed compounds such as benzo(a)pyrene being predominantly incorporated into airborne particles. For the four-ringed compounds such as pyrene, the partition is more equal. The extent of partition into airborne particles is dependent on the air temperature as well as the airborne particle loading. Yamasaki *et al*. (1982) proposed a temperature-dependent equilibrium constant. This is the ratio of the vapour phase (PAH) concentration (A) to the concentration in the particulate phase taken as the particle phase (PAH) concentration in air (F) divided by the concentration of total suspended particles (P):

$$\mathrm{K} = A/(F/P) = AP/F$$

This equilibrium ratio is strongly temperature dependent, and Foreman and Bidleman (1987) proposed the following relationship:

$$\log K = \log p^{\circ}_{L} + \log k'$$

Here, log p^{0}_{L} is the supercooled (conventionally referred to as sub-cooled) liquid phase vapour pressure of the compound and log k' is an intercept from a plot of log K versus log p^{0}_{L} for the class of compounds.

Table 2.2 Percentage of various PAHs in the vapour and particle phases determined from samples collected in Birmingham (Lim, 1999).

Compound	Number of rings	Vapour phase (%)	Particle phase (%)
Phenanthrene	3	98	2
Anthracene	3	97	3
Fluoranthene	4	95	5
Pyrene	4	93	7
Benzo(a)anthracene	4	12	88
Benzo(b)fluoranthene	5	4	96
Benzo(e)pyrene	5	2	98
Benzo(a)pyrene	5	<2	>98
Coronene	7	<2	>98

47. A more complex situation exists for particulate compounds formed by reversible chemical reactions. The best known example is that of NH_4NO_3, formed from the reversible reaction of gas phase NH_3 and nitric acid (HNO_3):

$$NH_3 + HNO_3 \leftrightarrow NH_4\ NO_3$$

Not only is the equilibrium ratio for the above process dependent upon temperature, it is also strongly affected by relative humidity above the deliquescence point of NH_4NO_3, since NH_4NO_3 then dissolves into an aqueous solution and its thermodynamic properties are changed. The existence of NH_4NO_3 in particles is strongly favoured by low temperature and high relative humidity; diurnal variations in the equilibrium between particulate NH_4NO_3 on the one hand and vapour phase NH_3 and HNO_3 on the other can be a result of normal daily cycles in humidity and temperature (Allen *et al.*, 1989). Sampling instruments that heat the incoming air tend to drive off semi-volatile constituents such as low molecular weight PAH, NH_4NO_3 and water.

2.3 Chemical composition of airborne particles

48. Airborne particles have a very diverse chemical composition that varies both in time and space. As indicated in Section 2.2, 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 SO_2 is typically present in fine particles, whereas silicon from the resuspension of soils and surface dusts is normally found in coarse particles. Due to the processes of condensation and coagulation, however, particles can become internally mixed. Such an internally mixed aerosol is a mix of particles containing components that have arisen from different sources. In contrast in externally mixed aerosols, particles have a composition that reflects the individual source. Coagulation and condensational growth processes tend to produce internally mixed particles.

2.3.1 Major components

49. Airborne particles contain both major and minor components. The major components, usually comprising at least a few per cent of the mass of particles, normally include the following:

- Sulphate – arises mainly as a secondary component from atmospheric oxidation of SO_2, although there may be a small primary component that arises from sea salt or mineral matter such as gypsum;

- Nitrate – normally present as NH_4NO_3, which results 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 – generally present in the form of ammonium sulphate ($(NH_4)_2SO_4$) or NH_4NO_3;

- Sodium and chloride – in sea salt;

- Elemental carbon – black, graphitic carbon formed during the high temperature combustion of fossil and contemporary biomass fuels;

- Organic carbon – carbon in the form of organic compounds, either primary, resulting from automotive or industrial sources, or secondary, resulting from the oxidation of volatile organic compounds (VOCs);

- Mineral components – crustal materials (rock and soil) are rich in elements such as aluminium, silicon, iron and calcium. These are generally present in coarse dusts that arise from, for example, wind-driven entrainment processes, quarrying, construction and demolition processes; and

- Water – water soluble components of airborne particles especially $(NH_4)_2SO_4$, NH_4NO_3 and NaCl – take up water from the atmosphere at high relative humidities, thereby turning from crystalline solids into liquid solution droplets. The transition occurs at a specific humidity known as the deliquescence point, at which dry crystals are exposed to increasing relative humidities (see Figure 2.3). There is, however, a hysteresis effect: upon a reduction in the relative humidity, water is lost only slowly and is retained at relative humidities well below the deliquescence point. This means that particles sampled from the atmosphere, even after drying at 40–50% relative humidity (as is customary before weighing), will still retain bound water, often representing a significant component of the mass.

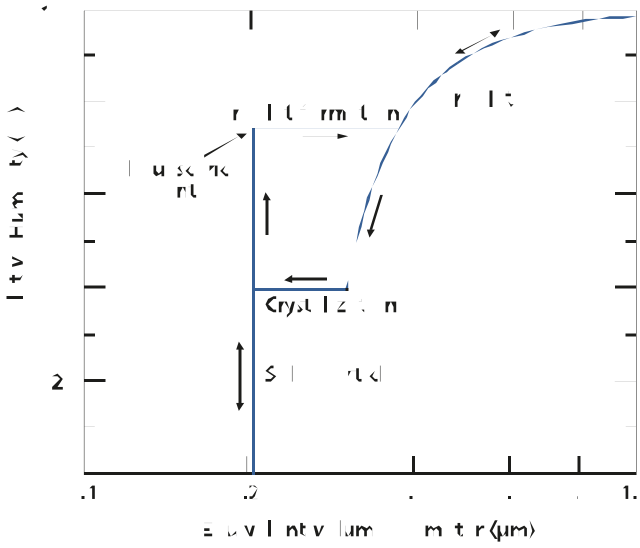
2.3.2 Minor components

50. Either in addition to or within some of the above major components there are many minor chemical components present in airborne particles. Their detection is often a function of the sensitivity of the analytical procedure. Minor components include the following:

- Trace metals – many metals such as lead, cadmium, mercury, nickel, chromium, zinc and manganese are used in metallurgical processes. Some occur as impurities or additives in fuels and others are used in industrial products. These and other uses cause emissions to the atmosphere, but concentrations are generally very small; and

- 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. Such organic compounds vary greatly in composition and include aliphatic and aromatic hydrocarbons, heterocyclics and oxygenates such as aldehydes, ketones and carboxylic acids. Generally speaking, organic compounds that arise directly from fuel combustion processes have a relatively high hydrogen to carbon ratio, whereas secondary organic compounds are more oxidised and polyfunctional carbonyl and carboxylic acids species are often present. To date, studies of specific organic compounds within airborne particles have mostly failed to account for more than 10% of the total mass of organic matter.

Figure 2.3 Equivalent volume particle diameter of a 10^{-14} g particle of NaCl as a function of increasing and then decreasing the relative humidity (based on Hinds, 1999).



2.4 Mass closure of airborne PM

51. The total mass concentration of particles in air can be determined by filtering a known volume of air and weighing the mass of particles collected by the filter. This is the principle behind both gravimetric techniques, such as the CEN reference method, and the TEOM instrument (see Chapter 5). In theory, it should be possible to analyse all of the chemical components within such a sample and, if all are accounted for, the sum of the masses of the individual components should equate to the mass of the sample determined by weighing. The concept of the sum of the components equalling the measured mass of particles is referred to as mass closure. In practice, mass closure for airborne particles has never been achieved since there are a number of components that cannot be measured adequately.

52. Specific problems in addressing mass closure include the following:

- As discussed above, under the usual conditions of weighing (standard protocols typically require humidities of 40% or 50%) particles retain some strongly bound water. There is no straightforward way of analysing the water content;

- Crustal materials have complex compositions and contain elements that cannot be readily analysed. For example, clay minerals in soils and rock have complex aluminosilicate structures and although measuring the aluminium and silicon content is relatively straightforward, the associated oxygen has to be estimated indirectly rather than analysed. Calcium and iron are also major components of some rocks and most soils, but they can be present in a variety of forms, including oxides and hydroxides (for iron) and sulphates and carbonates (for calcium). Without knowing the precise chemical form, it is difficult to use elemental analysis information for metals such as iron and calcium and empirical corrections are generally required; and

- As outlined above, it is not practicable to analyse all of the individual organic compounds and, therefore, techniques have been developed that analyse the two main forms of carbon: carbon present in elemental graphitic form and carbon present within organic compounds. Although no adjustment is needed to the mass of graphitic elemental carbon, it is necessary to adjust the mass of organic carbon upwards to allow for other elements such as hydrogen, oxygen and nitrogen present in the organic compounds. The recommended adjustment factors range from 1.2 for near-source environments to 1.8 for sites at which the majority of organic carbon is present as highly oxidised secondary components. Such factors are largely a matter of judgement and therefore open to significant uncertainty.

53. Attempts at mass closure for airborne PM have used a variety of approaches. The majority have used elemental analysis of a very wide range of components in order to analyse the major constituents. Inevitably, however, some reconstruction is needed to estimate the mass of crustal/soil particles, the organic compound mass from the organic carbon concentration and the quantity of bound water, which is often simply estimated by determining difference from the mass of the other components.

Table 2.3 Adjustment factors used in mass closure (from Harrison *et al*., 2003).

Analyte	Conversion to	Numerical factor
Sulphate	$(NH_4)_2SO_4$* hydrate	1.38 1.29
Nitrate (fine)	NH_4NO_3 hydrate	1.29 1.29
Nitrate (coarse)	$NaNO_3$ hydrate	1.37 1.29
Chloride	NaCl	1.65
Calcium	$CaSO_4.2H_2O$	4.30
Iron	Soil/road dust	5.50 (roadside) 9.00 (background) 3.50 (roadside increment)
Elemental carbon	Elemental carbon	1.00
Organic carbon	Organic compounds	1.30 (roadside) 1.40 (background) 1.20 (roadside increment)

54. A simplified approach developed within the UK is based upon the analyses and conversion factors given within Table 2.3 (Harrison *et al*., 2003). The basis of this method is to assume that sulphate is present as (NH4)2SO4; nitrate as NH4NO3 and NaNO3 in fine and coarse particles, respectively; and chloride as NaCl. As outlined above, a factor is used to convert the organic carbon measurement to a mass of organic compounds. Calcium is assumed to be present in the form of gypsum and iron is used as a tracer for other entrained crustal/road dust materials. The factors by which iron concentrations are increased are determined empirically from the data and increase between roadside samples and urban background, reflecting a greater enrichment of iron in traffic-related particles. Both sulphate and nitrate are assumed to be associated with strongly bound water and their masses are increased by an empirically estimated factor to allow for this. Use of this method has accounted for around 100% of measured particle mass and a high proportion of the variance in daily mass concentrations for both roadside and urban background locations.

2.5 Source apportionment

55. Source apportionment refers to the quantitative attribution of airborne pollutant concentrations to specific source categories. It, therefore, deals with particles measured in the air. This contrasts with source inventories, which quantify the amounts of pollutants emitted but take no account of either dispersion conditions and, therefore, effects on ground-level concentrations – or secondary formation. The results of source apportionment studies are key to targeting cost-effective mitigation measures at those pollutant sources making the greatest contributions to air pollution.

2.5.1 Dispersion modelling

56. One means of pollutant source apportionment is to construct a spatially disaggregated inventory of emissions of that pollutant and then model dispersion of the emissions. By such means the concentration attributable to each emission source can be estimated. This procedure can be very effective in the case of pollutants such as SO_2, which have well defined and quantified sources. However, for airborne particles, emissions inventories tend to be incomplete or uncertain and dispersion modelling alone is unlikely to provide a very good estimate of airborne particle concentrations and thus source apportionment.

2.5.2 Receptor modelling

57. Receptor modelling refers to the use of measured air quality data to achieve source apportionment of airborne material such as particles. A number of different approaches have been used for receptor modelling of airborne PM. These include the following:

- In its Third Report, in 1996, the QUARG estimated the proportion of airborne particles derived from road vehicle emissions by examining the correlations between PM_{10} and $PM_{2.5}$ and either NO_x or carbon monoxide (CO), both of which are assumed to arise almost wholly from road traffic emissions within urban areas. The assumption on which this work was based was sounder at the time of the QUARG work than it would be now: these days a greater proportion of urban emissions of NO_x and CO arise from non-traffic sources. Linear regression analysis gives rise to a relationship in the form:

  $$PM_{10} = mNO_x + \mathrm{c}$$

  The intercept, c, relates to that part of PM_{10} that does not vary with NO_x emissions and, therefore, is assumed not to arise from road traffic. The road traffic contribution is, therefore, determined by difference (PM_{10} – c).

- Using major components as source indicators. The receptor modelling method adopted by APEG (1999) used sulphate as a surrogate for all secondary inorganic particles and then black smoke (later NO_x) as a surrogate for emissions from combustion sources that were largely but not solely road traffic. They then estimated scaling factors to account for the unmeasured part of the pollution from these sources. The third category of 'other', mainly coarse, particles was estimated by the difference. In the simplified mass closure method outlined in Section 2.4, this method is extended to include sulphate that arises mainly via secondary formation from SO_2 oxidation, nitrate from NO_x oxidation, elemental and organic carbon representing predominantly the emissions from combustion processes, sea salt and two types of crustal/soil/road dust particles indicated by calcium and iron. Furthermore, the organic to elemental carbon ratio can be used to distinguish between secondary and primary organic carbon.

- Multi-element analysis and multivariate statistical methods. There are a number of related source apportionment methods that depend upon the collection of a large number of sequential, normally daily, samples of airborne particles that are analysed for a wide range of chemical elements, often together with major ions and possibly some organic compounds (Hopke, 1985). The dataset is then analysed using a multivariate statistical method designed to recognise those components with a common temporal variation and with the capacity to aggregate the different chemical components into a smaller number of 'factors' that together account for a large proportion of the variance within the dataset. Thus, for example, sulphate, nitrate and ammonium are often identified within a single factor that corresponds to long-range transport of secondary components. Until recently road traffic emissions were generally identified through a factor heavily influenced by lead and bromine, reflecting the use of lead antiknock additives and brominated scavengers in petrol, a practice now discontinued in the UK. Although the method will aggregate individual chemical elements into factors with common sources, it requires expert judgement to associate the factors within given source categories. This is often dependent upon the association of trace elements with emissions from specific sources. For example, arsenic and selenium have typically been used as tracers for coal combustion sources, whereas vanadium and nickel indicate emissions from fuel oil combustion.

Although this technique has, in the past, generated relatively clear-cut quantitative information about the source apportionment of airborne particles, nowadays it appears to be far less effective. As a result of pollution control measures, trace elements have reduced greatly in concentration and now often arise in very small amounts from multiple sources. Additionally, elemental tracers such as lead, which in the past were very effective as source markers, are now no longer in use and inorganic elements do not provide a ready means of identifying road traffic emissions.

- Organic source tracers. Research in the United States (US) has demonstrated that certain trace level organic compounds can be very effective tracers of specific sources (Schauer *et al*., 1996). Thus, for example, hopanes and steranes, – complex substances present at low levels in petroleum fuels – are used as tracers of hydrocarbon fuel combustion (Fraser *et al*., 2003). Certain PAHs can be related to individual combustion sources, for example retene arises mainly from the combustion of wood. The application of such organic source tracers in a quantitative manner requires very detailed information on their abundance in emissions from all major source categories. Currently, they have only been applied in a detailed way to the source apportionment of PM in California; their use in Europe has yet to commence.