

NPL REPORT AS 43

**Airborne particles – a broad
review of issues for the
NANOAIR project**

Paul Quincey

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July 2009

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a broad review of issues for the NANOAIR project

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

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Approved on behalf of the Managing Director, NPL
by Martyn Sene, Director, Operations Division

Executive Summary

This review describes the main issues relating to airborne particles, especially in outdoor (ambient) air.

Section 1 outlines the main features of ambient airborne particles, in terms of their size and bulk composition.

Section 2 describes the sources of particles found in the atmosphere. These are diverse and variable, including natural sources (such as mineral dust and sea salt), anthropogenic sources (such as vehicle and industrial emissions), and secondary particles formed from gaseous precursors (such as ammonium nitrate).

Section 3 describes the most common measurement parameters used to characterise airborne particles, such as PM_{10} , $PM_{2.5}$, number concentration, size distribution, and chemical composition. The limitations and associated measurement uncertainties of these parameters are emphasised. The inconsistency and inappropriateness of many of the measurement techniques can be a significant barrier to implementing effective mitigation measures and to health effects studies.

Section 4 describes the current position regarding the health effects of airborne particles on human health. While there is consensus that the health effects of exposure to ambient particles are substantial, there is little consensus on the specific aspects of the particles that cause the effects, beyond that fine particles (below around $2.5\ \mu\text{m}$ in diameter) have a greater effect than that of coarse particles.

New techniques for characterising airborne particles are likely to have a valuable role in clarifying the nature of particles in the air at any given location and time, the properties of the particles that cause health effects, and consequently the policies that should be followed in order to reduce the health effects of particles on the population.

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1.0 Introduction

1.1 Scope

This study gives an up-to-date summary of the main issues relating to airborne particles, especially in regard to the properties of the particles that are most important for human health effects. This is an active area of research, currently characterised in key areas by inconsistent results, so the emphasis will be more on highlighting the problematic areas than on presenting conclusions.

There are many major review studies, by authoritative national or international groups, of health effects from particles – these will be referenced, but not reported in detail. These reviews tend to understate the difficulties in obtaining reliable and consistent measures of particles that are used in the studies.

There is a strong emphasis within this study on particles in ambient (ie outdoor) atmospheres, rather than indoor (domestic) or industrial workplace situations. This is because:

- Ambient air contains a complex and variable mixture of particle types, from both “natural” and man-made sources - it is not a simpler alternative to indoor air;
- Except in specialised cases, ambient particle concentrations will form the background to indoor concentrations, and can be of similar scale, so they are always relevant;
- Indoor (especially industrial) atmospheres depend strongly on the details of the processes being used, so that it is difficult to describe representative results for indoor situations within a reasonable sized document;
- There is much more research available for health effects of ambient particles than for particles in other environments.

The study will focus on the situation in Europe rather than globally, and some illustrations will be used from the United Kingdom.

1.2 General characteristics of airborne particles

Even in remote areas of land free from local sources of pollution, airborne particles will vary greatly in size distribution, composition and concentration over time and from place to place. There is no “typical” background, though of course average values can be obtained.

In the broadest sense, particles can be characterized by their size and their composition.

1.2.1 Size range of ambient air particles

The largest particles to remain suspended in air for an appreciable time before settling out are around 100 μm in diameter. This sets the relevant upper size limit. The low size limit is more arbitrary, as there is a continuum of sizes between large organic molecules and particles forming through condensation, but can be taken for practical purposes in this report to be around 10 nm.

Within this range, ambient particles typically fall into three distinct populations, shown in Figure 1. These are given a variety of names, and they are here termed “transient nuclei” (up to roughly 100 nm), “accumulation mode” (roughly 100 nm to 1 μm) and “coarse mode” (above roughly 1 μm). The populations arise from distinct mechanisms.

The larger, coarse particles are typically those that are generated at that size by mechanical processes, such as wear of crustal rocks and the suspension of soil, mechanical wear, volcanic particles, and salt particles left by evaporated sea spray.

The smallest, transient nuclei particles are quite different, being a mixture of carbonaceous combustion products (ie “soot”) – shown as primary particles in the diagram, particles formed by condensation from hot vapours (such as from metallurgical processes), and particles such as ammonium sulphate formed by homogeneous nucleation from gaseous precursors.

These transient particles tend to grow in size over timescales of minutes to days by condensation (ie collection of molecules by the particles) or aggregation (ie the joining together of transient particles, such as soot particles forming chains). This is the longer lasting accumulation mode.

It can be seen that industrial nanoparticles, taken to mean particles smaller than 100 nm, would affect only the numbers of transient nuclei.

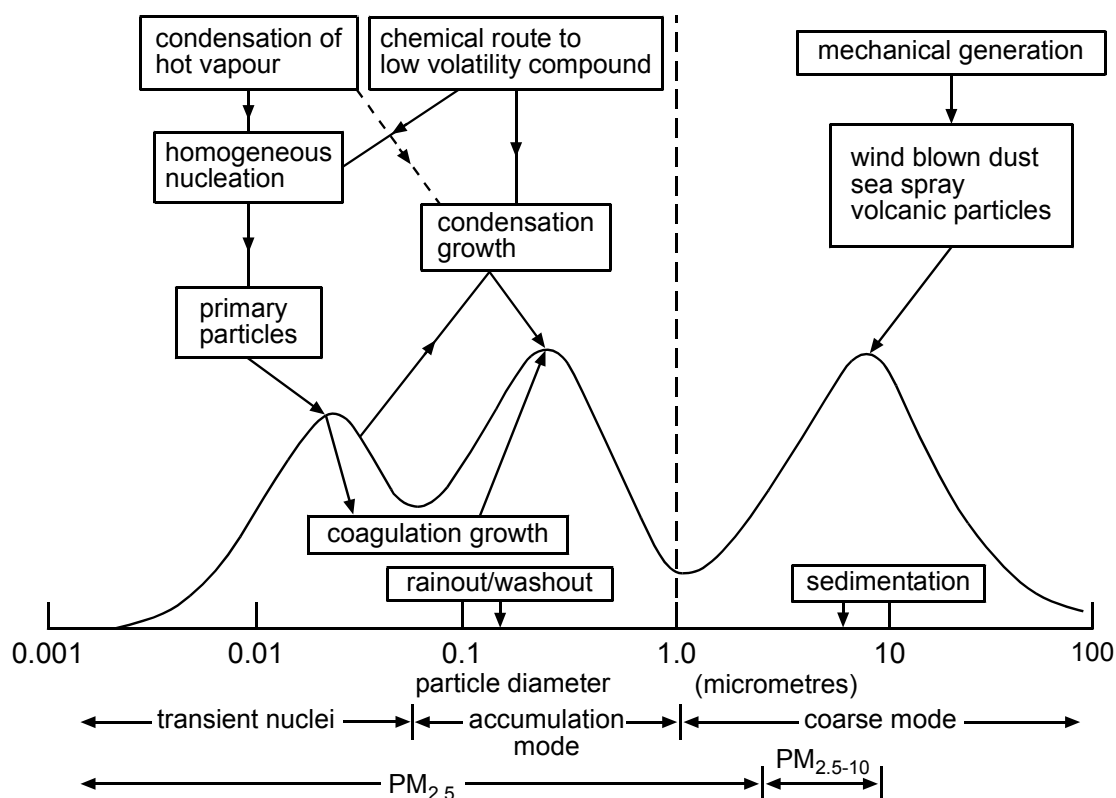


Figure 1: Schematic diagram of size distribution of ambient airborne particles (taken from [1]).

The y-axis of Figure 1 is highly schematic, representing neither numbers of particles nor volume (or mass) of particles. The great majority of particles by number are in the sizes below 200 nm, whereas the mass of particles is dominated by particles larger than this, especially in the coarse mode.

1.2.2 Composition of ambient air particles

It cannot be overemphasised that the composition, size and concentration of ambient air particles will change dramatically and rapidly with wind speed, wind direction and local activities, as well as more slowly with diurnal, seasonal and long range factors.

Composition is almost always expressed as the mass fraction of particles up to a certain upper size, for example 2.5 µm or 10 µm (which give the commonly used PM_{2.5} or PM₁₀ values described in Section 3 below). The PM_{2.5} or fine fraction is a good approximation to the

combined transient nuclei and accumulation modes. It must be remembered that mass fractions will be strongly biased towards the larger particles in the size range.

Some representative compositions for roadside and urban background locations are shown in Figures 2 to 5 (from the TRAMAQ study, taken from reference [1]). Coarse particles in this case refers to the size range from 2.5 to 10 μm .

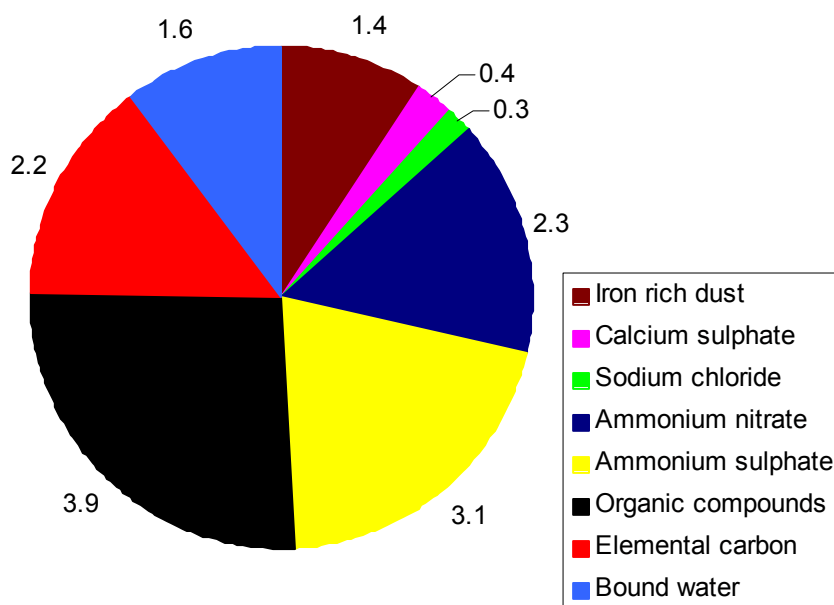


Figure 2: Fine particles at urban background sites

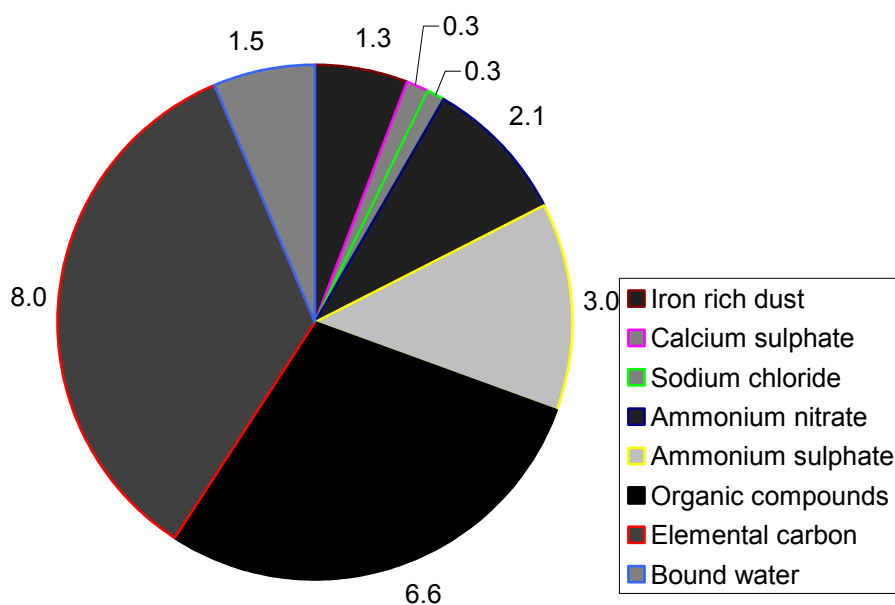


Figure 3: Fine particles at roadside sites

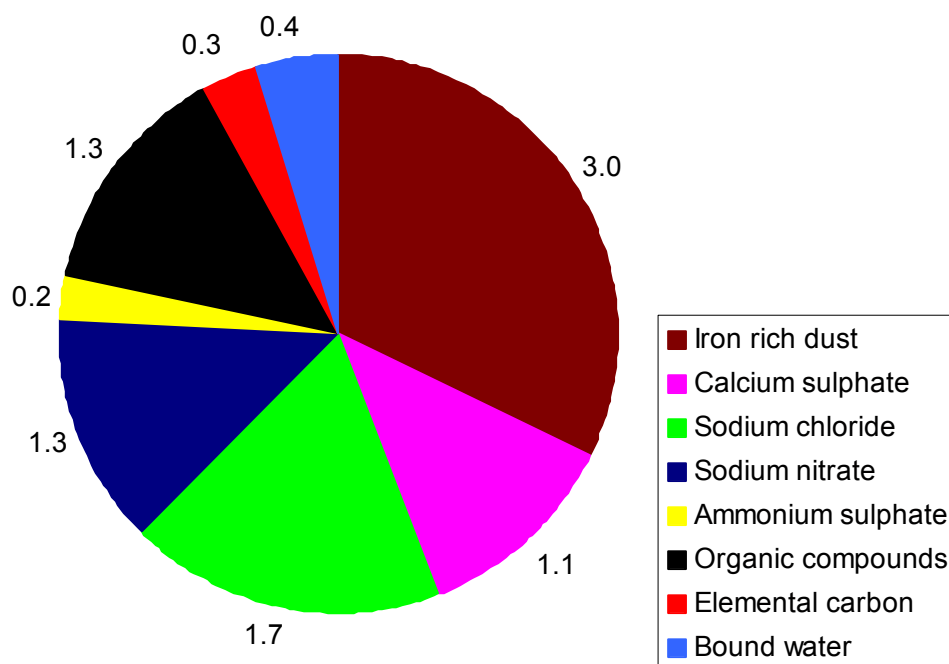


Figure 4: Coarse particles at urban background sites

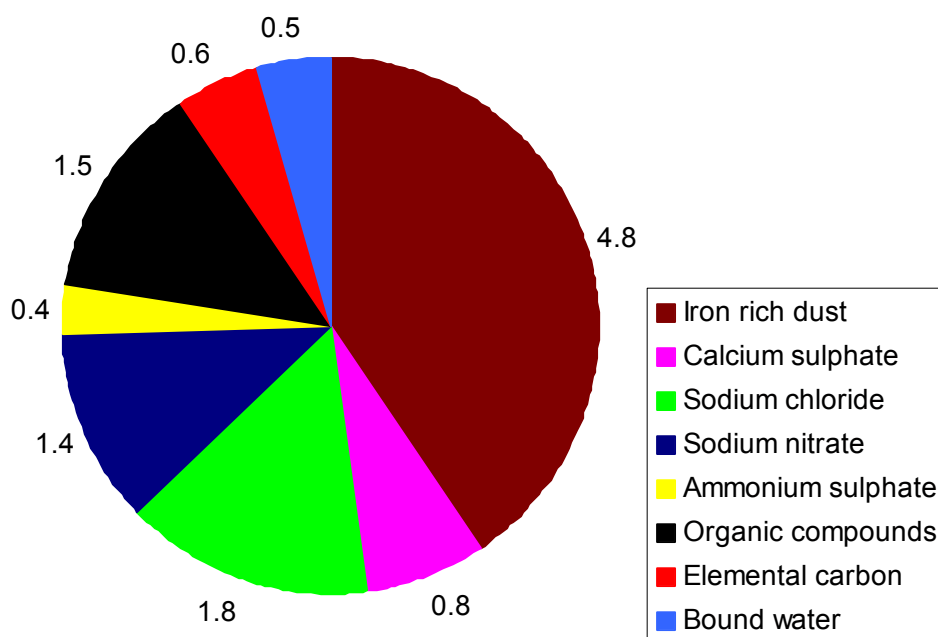


Figure 5: Coarse particles at roadside sites

To summarise the main points to note:

At urban background sites, iron rich dusts, sodium chloride and calcium sulphate (gypsum) together form about 60% of the coarse fraction, but only about 15% in the fine fraction, indicating that these components are present predominantly as coarse particles. Sodium nitrate is also present predominantly as coarse particles.

On the other hand, ammonium sulphate, ammonium nitrate and elemental carbon (soot) are present predominantly as fine particles. Organic compounds are present in similar proportions in both size fractions.

The most notable differences at roadside sites are the increase of iron rich dust in the coarse fraction, thought to be from a combination of mechanical wear within vehicles and resuspension of dust from the road surface, and the increase of elemental carbon and organic compounds in the fine fraction, from vehicle exhaust emissions.

1.2.3 Concentration of ambient air particles

The effect of a local or industrial source of particles must be seen in the context of the ambient concentrations. Indicative long-term average concentrations are:

	Urban roadside	Urban background	Rural
PM ₁₀	35 µg/m ³	20 µg/m ³	15 µg/m ³
PM _{2.5}	25 µg/m ³	15 µg/m ³	10 µg/m ³
Particle number	100,000 cm ⁻³	20,000 cm ⁻³	10,000 cm ⁻³

Table 1: typical ambient air particle concentrations

The measured parameters are described in more detail in Section 3. Hourly average values can differ from these averages by a large factor because of meteorology and local factors.

2.0 Sources of airborne particles

2.1 Primary and secondary particles

Airborne particles can be classified as either primary or secondary, depending on their formation:

- Primary particles are emitted directly into the environment as particles, from both natural sources such as wind-blown soil and sea salt, and anthropogenic sources, such as combustion processes and quarrying. Smaller particles may aggregate over time, while larger ones will settle out of the air through gravity.
- Secondary particles are formed within the atmosphere as a result of chemical reactions that lead to the formation of substances that condense into the solid or liquid phase. Examples are ammonium nitrate and certain organic aerosols.

Depending on atmospheric conditions and local sources, secondary particles can be comparable in quantity with primary particles, especially at lower size fractions, as can be seen from the Figures above.

The classification into primary and secondary particles is not entirely simple as, for example, sodium nitrate is formed from the reaction of gaseous N₂O₅ (formed ultimately from NO₂ and ozone) with solid sodium chloride. The essential point is that the population of particles in the atmosphere cannot simply be modelled by the dispersion of emitted particles from various sources. Any realistic assessment of the particle population needs to take into account gaseous emissions and chemical processes.

2.2 Natural sources

The evaluation of natural sources of airborne particles has recently received impetus because of an increased emphasis within the 2008 Air Quality Directive [2] on Member States being allowed to disregard breaches of PM limit values when these are caused by “natural” episodes [3].

Wind blown, long-range, transported mineral dust and sea salt are the most important natural sources, but there are many other sources with potentially significant effects that can be attributed to natural sources, though the boundaries between natural and anthropogenic become a little blurred.

2.2.1 Mineral dust

Mineral dust mainly affects European countries near to the Mediterranean Sea, close to the Sahara and Sahel deserts, though Saharan dust episodes can be observed in the United Kingdom. IPCC [4] estimated emissions across the Northern Hemisphere of 1800 Tg/yr for soil dust, and episodes are clearly visible from satellite photographs, such as Figure 6. More than 95% of these emissions (by mass) are in the coarse category, $> 1 \mu\text{m}$ in size.

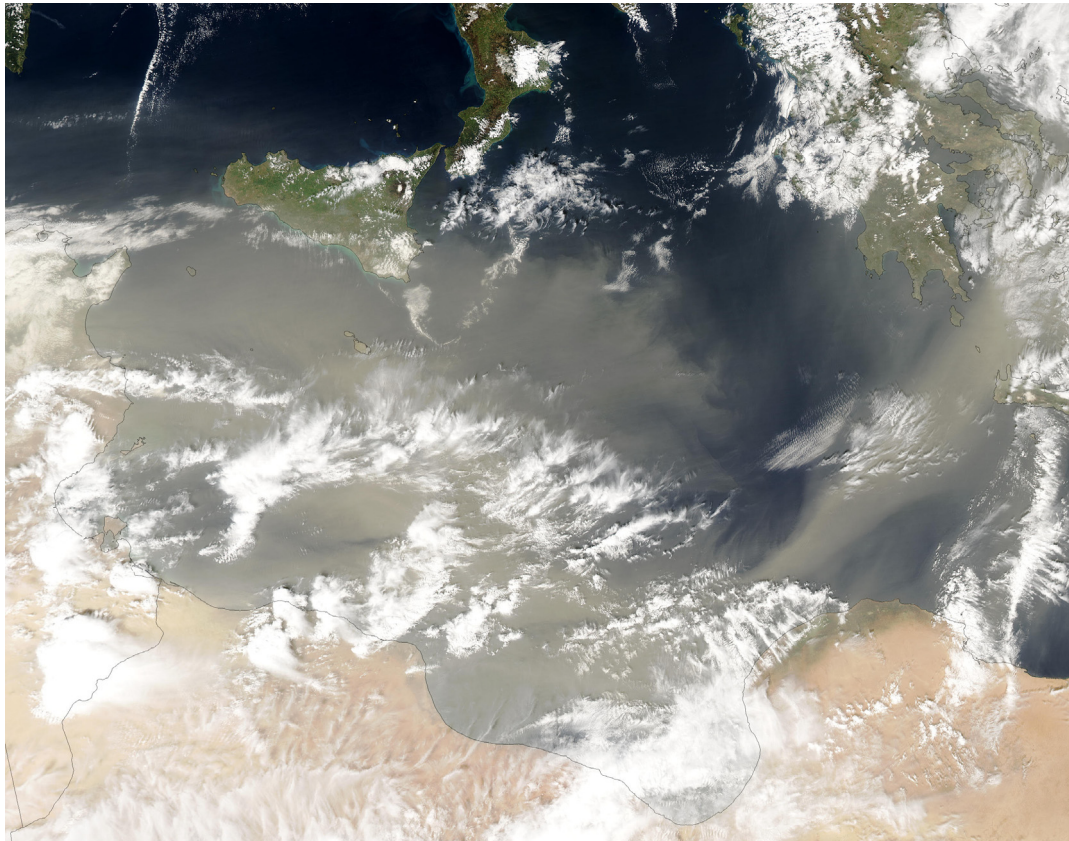


Figure 6: Mineral dust in the Mediterranean visible from space (Courtesy of NASA).

Mineral dust particles are mainly composed of aluminium silicates, silicon dioxide (quartz), calcium carbonate, and magnesium carbonate. Iron compounds are also present in significant amounts.

2.2.2 Sea salt

The impact of sea salt particles, formed by the evaporation of sea spray, is geographically more widespread than mineral dust, affecting predominantly coastal regions, though the effects can extend inland. IPCC [4] estimated emissions across the Northern Hemisphere of 1500 Tg/yr for sea salt. Like mineral dust, more than 95% of these emissions (by mass) are in the coarse category, $> 1 \mu\text{m}$ in size.

The composition of fresh sea salt particles can be estimated from average sea water composition. The principal component ions are:

Chemical ion	Molar %	Weight %
Chloride Cl^-	48.8	55.0
Sodium Na^+	41.9	30.6
Magnesium Mg^{++}	4.8	3.7
Sulphate SO_4^{--}	2.5	7.7
Calcium Ca^{++}	0.9	1.2
Potassium K^+	0.9	1.1

Table 2: Average sea water composition.

When distinguishing between sea salt and mineral dust particles, the usual assumption is that all the sodium ions in a sample are of marine origin, and from their concentration the sea salt contribution of chloride, sulphate, magnesium, calcium and potassium can be calculated using the values in Table 2. The remaining calcium concentration, with the sea salt contribution removed, is seen as a convenient tracer for mineral dust.

The other natural sources listed in the sections below have less overall effect on the ambient particle population, though they can have significant seasonal, temporary or local effects. There is also some ambiguity about whether some should be classified as natural or anthropogenic.

2.2.3 Primary biological aerosol particles (eg pollen, spores and plant fragments)

The presence of biological aerosol particles is typically highly seasonal, with very low emissions in winter. Active periods may account for 5% of PM_{10} . The sources have been summarised by Jaenicke [5].

Pollen, spores, bacteria and viruses are present in the atmosphere as individual structural units with distinct sizes and properties. Pollens are typically larger than $30\text{ }\mu\text{m}$, with a few exceptions such as birch pollen as small as $10\text{ }\mu\text{m}$. They can contribute greatly to the mass concentration of total suspended particles, but contribute little to the usual size fractions monitored, ie PM_{10} and $\text{PM}_{2.5}$.

Spores such as fungal spores and those from mosses and ferns are smaller than pollens with a size of typically a few micrometres. They can be present at concentrations of up to a million per cubic centimetre. They can contribute a few $\mu\text{g}/\text{m}^3$ to measured mass concentrations over short periods.

Bacteria and viruses are smaller than spores by two or three orders of magnitude, and their numbers are such that their effect on particle mass concentrations is negligible.

In contrast to the structural units, plant fragments have a much larger size range, and less can be said about them with any certainty. Pollen fragments or other plant debris could form a significant fraction of organic carbon in some circumstances, but overall contributions do not appear to be large.

2.2.4 Forest fires

Forest fires can have a significant but infrequent effect on particle concentrations, those in Portugal in the summer of 2005 being an example. Their effects are combustion products similar to those of biomass burning. It is debatable whether forest fires in Europe can be considered natural.

2.2.5 Volcanic eruptions, seismic and geothermal activities

Volcanic activity will have a major but infrequent effect in relevant areas of Europe such as Iceland, Sicily and the Canary Islands. Fine fly ash can be an important source of PM_{10} in local cities. Emissions of sulphur dioxide can also influence the formation of secondary sulphate particles.

2.2.6 Secondary organic aerosol

Terpenes emitted by vegetation such as forests are known to contribute to organic aerosol formation in Europe. This is an active area of research, and the effects are not known in detail. However, the effects are expected to be small compared to those of the main natural sources.

2.3 Anthropogenic primary emissions from transport

The presentation of sources of airborne particles from human activities will be separated into primary sources, subdivided into transport-related and stationary source-related, and sources of the precursors of secondary particles.

2.3.1 Road transport exhaust emissions

Vehicle particle emissions, especially from diesel engines, are the most closely studied and regulated type of emissions, though there are still considerable uncertainties about the total quantities involved in actual situations.

In terms of particle numbers, immediate diesel combustion products are primarily in the nucleation mode of particles below 100 nm in size. These particles are mainly lower volatility organic and sulphur compounds, with some solid carbon and metallic particles. By the time they reach the exhaust pipe the particles tend to be carbonaceous agglomerates, with soot spherules of diameters 15-30 nm, that have been coated with absorbed or condensed organic compounds, joined together as amorphous strings to form accumulation mode particles.

The majority of the emitted mass is in the accumulation mode particles, with a minority (5-20%) in coarse particles that are material that has been previously deposited on the cylinder and exhaust system surfaces.

European legislation has required drastic reductions in particle emissions from both petrol and diesel vehicles, and actual emissions are a sensitive function of the vehicle fleet composition, state of repair and other factors.

2.3.2 Tyre and brake wear

Relatively small amounts of data exist for tyre and brake wear. Tyre wear particles are typically coarse, and the emissions are composed of elemental carbon, hydrocarbons, zinc, iron and other inorganic compounds containing sulphur, silicon and calcium. Zinc is a useful chemical marker for tyre wear.

Emissions from the brake lining and the brake surface are typically smaller than from tyre wear. The particles have been found to consist of various organic compounds, elemental carbon, and inorganic compounds containing silicon, barium, iron, magnesium, phosphorus and chlorine.

2.3.3 Resuspension

Passing vehicles will resuspend loose, deposited particles on the ground both through the action of the tyres on the road surface and through air turbulence. Again, fewer data are available than for exhaust emissions, and clearly quantities will be highly variable depending on conditions. For the purposes of this study, the composition of the resuspended material will be broadly the same as that of the ambient particle population, so this source is relatively unimportant.

2.3.4 Non-road transport

Rail, aircraft and shipping, as well as other non-road mobile machinery, also contribute to primary emissions of particles. In general these do not produce fundamentally different

combustion products to those from road transport. The relative emissions depend strongly on the machinery and circumstances.

2.4 Anthropogenic primary emissions from stationary sources

Stationary sources in this context means all non-transport sources. The major sources are fuel combustion and certain industrial processes. Agricultural processes and waste incineration are less important sources.

2.4.1 Fuel combustion

Fuel combustion sources include the relatively small number of large power stations and the large number of small residential combustion units, with industrial and commercial scale plants falling between the two categories.

Emissions of particles depend very much on the fuel used and the type of unit. In the United Kingdom, emission factors of PM₁₀ emission from coal vary from 319 g/tonne in power stations to 2,500 g/tonne in commercial-scale plants, to 10,400 g/tonne in domestic combustion (3,594 g/tonne for anthracite). This reflects both the lower efficiency of combustion in domestic units and the use of abatement systems on power stations that reduce the number of particles in their emissions. Coal burning in the domestic sector was estimated to have contributed a similarly large amount of primary PM₁₀ to power stations within the United Kingdom in 2001, even though the power stations used around 30 times more coal.

All energy intensive industries will therefore contribute combustion particles to the atmosphere. It is hard to be specific about their composition and size. In general, particles from less efficient combustion processes would be expected to consist mainly of carbon. Particles from larger, more efficient combustion processes would be expected to contain more inorganic matter resulting from the mineral content of the fuel, for example fly ash, which may contain metals.

2.4.2 Industrial processes

Non-combustion industrial particle emissions mainly occur as a result of:

- Grinding, crushing or abrading of larger-sized material, for example in cement clinker grinding, expected to produce mainly coarse particles; and
- Recondensation of volatile matter from heated materials, for example in glass and non-ferrous metal furnaces, expected to produce mainly fine particles.

The largest non-combustion PM₁₀ emissions in the United Kingdom are found to be from the iron and steel industry, cement production, lime works, brick manufacture and wood products manufacture.

The composition is expected to be inorganic matter chemically similar to the raw materials or products of the process.

Other processes can of course produce significant emissions on local scales, and this will be especially important when specialised plants are manufacturing specific chemicals.

2.4.3 Mining, quarrying and construction

These are known to be significant sources, but they are poorly quantified. The particles are likely to be predominantly coarse, with composition similar to that of the material being worked.

2.4.4 Agriculture

Particle emissions as a result of agriculture are also poorly quantified, and come from activities such as ploughing and animal housing, especially for poultry. Agriculture is more significant because of its contribution to secondary particle formation via ammonia, described below.

2.4.5 Summary of relative contributions for the United Kingdom in 2001

The scale of anthropogenic particle emissions at different sizes for one EU Member State can be gauged from the table below, taken from the AQEG report [1]. The figures are based on the national emissions inventory.

Sector	% of UK emissions			
	PM ₁₀	PM _{2.5}	PM ₁	PM _{0.1}
Electricity generation:				
Coal	8.7	6.7	4.0	4.2
Other fuels	1.1	1.9	2.4	2.6
Industrial/commercial combustion:				
Coal	3.0	3.4	2.2	1.3
Natural gas	2.1	3.6	5.0	6.1
Other fuels	3.8	3.6	3.0	3.2
Domestic combustion:				
Coal	7.0	4.7	5.4	1.0
Smokeless fuels	3.6	1.7	0.4	0.3
Wood	3.9	4.9	2.8	1.9
Natural gas	2.3	4.1	5.7	1.3
Other fuels	0.4	0.5	0.7	0.3
Industrial processes:				
Iron and steel	4.0	4.5	4.0	4.8
Cement and lime	1.8	1.7	1.1	1.1
Glass, bricks and ceramics	2.1	2.7	3.5	4.2
Quarrying	11.4	5.9	2.3	0.0
Construction	2.4	1.3	0.7	0.0
Other	5.0	5.3	6.2	5.5
Transport				
Road transport – petrol	1.7	2.4	2.8	3.2
Road transport – diesel	15.2	24.1	31.3	44.3
Road transport – brake/tyre wear	4.9	4.8	1.2	2.3
Off-road vehicles	4.0	5.5	6.7	3.6
Other transport	1.1	1.7	2.2	1.0
Waste disposal:				
Foot and mouth pyres	2.1	1.5	1.6	0.3
Other	0.8	1.5	2.0	0.6
Agriculture	7.6	2.2	2.8	6.8

Table 3 Contribution to UK particle emissions by source sector and size fraction in 2001.

2.5 Anthropogenic sources of secondary particle precursors

2.5.1 Inorganic secondary particles

The principal gaseous precursors for secondary inorganic particles are sulphur dioxide, oxides of nitrogen (NO_x) and ammonia. The principal solid products are ammonium sulphate, ammonium nitrate, and, via reaction with sodium chloride particles, sodium nitrate. As seen in Section 1.3, these can form a major fraction of the airborne particle population, especially in the fine fraction.

The main sources of sulphur dioxide are the combustion of solid fuel and petroleum products, especially coal burning, arising from the presence of sulphur in the fuel.

NO and NO₂ are readily interconverted within the atmosphere by photochemical processes, and they are collectively termed NO_x. NO_x is created in fossil fuel combustion by the oxidation of nitrogen in the air. The major sources are generally road transport and power generation.

The dominant source of ammonia emissions is agricultural animal waste, where it is a product of the breakdown of urea and uric acid.

By their nature, secondary particle concentrations are much less localised than primary particle concentrations.

2.5.2 Organic secondary particles

In general terms, secondary organic particles are formed by the oxidation of volatile organic compounds (VOCs) such as hydrocarbons, of which many hundred species may be involved. Oxidation to the aldehyde, ketone or alcohol groups, for example, makes the products less volatile and more soluble in water. Further oxidation can introduce additional functional groups that make the products even less volatile and more soluble, and therefore form particles. The situation is made more complex because oxidation mechanisms can also lead to the fragmentation of the molecules, so that ultimately all the carbon in the VOCs is converted to carbon dioxide.

The most important VOCs in the production of secondary particles are large, cyclic, unsaturated compounds such as monoterpenes (for example α - and β -pinene) and aromatic hydrocarbons (for example toluene and the xylenes). The monoterpenes are primarily emitted by vegetation (trees), and are therefore from natural sources, whereas the aromatics are mainly of anthropogenic origin from road transport emissions.

3.0 Measurement of airborne particles

Having established the complexity and variability of airborne particles, it must be appreciated that studies on the health effects of particles, especially epidemiological studies, are limited by the types of measurement that are available. For historical and practical reasons, these give measures of airborne particles using greatly simplified parameters.

3.1 Mass concentration (eg PM₁₀ and PM_{2.5})

Most current legislation for air quality, and emissions relating to airborne particles, refers to the mass concentration of the particles – the mass of the particles within a specified volume of air. Historically this arose as a simple method of quantifying airborne particles by sampling a known volume of air onto a filter, and measuring the change in mass of the filter by weighing (gravimetry).

Early measurements made no concerted attempt to limit or specify the size range of particles to be collected and weighed, and the sample was described as Total Suspended Particulates. In practice, an upper size limit for any given sampling device is usually set by impaction – the inability of larger particles to follow the path of the air stream without colliding with and sticking to the walls, shown schematically in Figure 7. Fibrous filters are in general very good at collecting small particles, which come into contact with the fibres by diffusion, so that there is effectively no lower size limit for the collected particles, though these small particles will have a negligible effect on the collected mass.

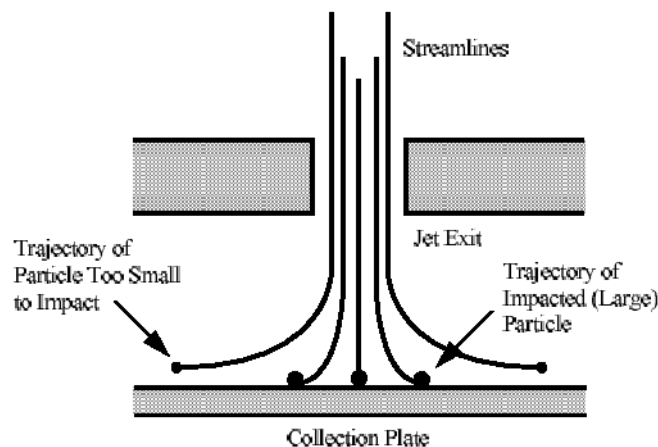


Figure 7: Schematic diagram of particle impaction.

Systematic attempts to control the upper size limit were linked to ISO 7708 *Air quality -- Particle size fraction definitions for health-related sampling*, which was published in 1983. This set conventions for the size ranges of particles relevant to human health:

- **Inhalable fraction:** The mass fraction of total airborne particles which are inhaled through the nose and mouth;
- **Thoracic fraction:** The mass fraction of inhaled particles penetrating beyond the larynx. The median cut-off particle diameter is 10 μm .
- **Respirable fraction:** The mass fraction of inhaled particles that penetrates to the unciliated airways deep in the lung.

The "**high risk**" respirable convention is used if it is desired to protect children or sick persons. The particle cut-off median diameter is 2,5 μm .

The "**healthy adult**" respirable convention is used if it is desired to protect healthy adults. The particle cut-off median diameter is 4,25 μm .

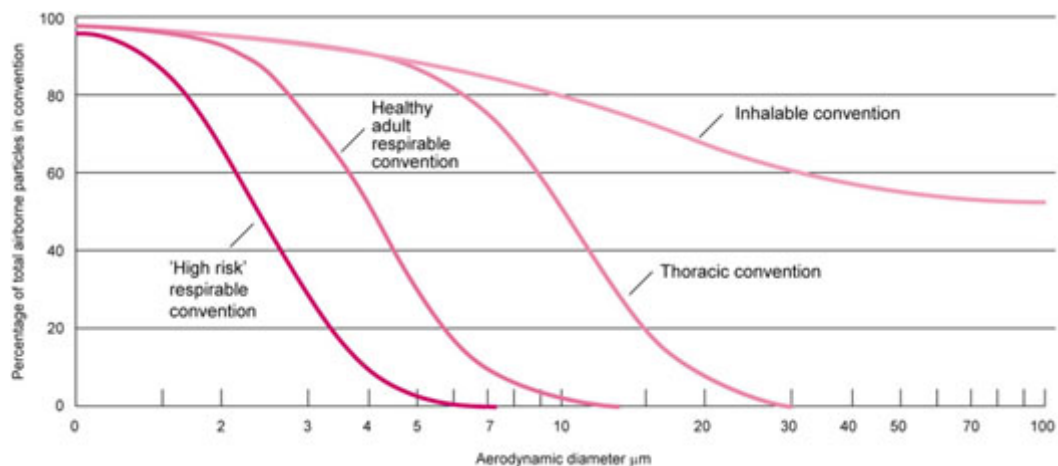


Figure 8: Particle size conventions relating to human breathing (from ISO 7708).

Since these conventions were agreed, the majority of sampling inlets were designed to collect the fraction of particles less than 10 μm in size, termed PM_{10} , or the fraction less than 2.5 μm in size, termed $\text{PM}_{2.5}$, either by using impactor systems or cyclones.

There are two important points to note at this point. Firstly, as can be seen from Figure 1, the PM_{10} upper size limit falls quite centrally in the coarse fraction of the particle population in the atmosphere. As particles around this size contribute significantly to the total mass collected, the performance of the size-selective inlet will be important to the result. This performance is typically affected by the exact flow rate through the inlet, the build up of impacted material, and the application of grease to the impactor. By chance, the $\text{PM}_{2.5}$ upper size limit coincides roughly with the boundary between the fine and coarse fractions, where concentrations are relatively low, so that this problem is reduced, but not eliminated.

Secondly, no size-selective inlet has an exact cut-off size. The inlets will have a cut-off curve of the form shown in Figure 8, which will again depend on the exact design and circumstances of the inlet. While early designs of inlet attempted to match the curves presented in ISO 7708, it has become accepted within Europe that the desired cut-off curve is instead defined by adopting a small number of "reference" inlet designs, which, with their prescribed operating procedures, are deemed to sample the correct fraction. Again, the inlet cut-off curve is more critical for PM_{10} than for $\text{PM}_{2.5}$.

These points highlight some basic problems with PM_{10} and $\text{PM}_{2.5}$ measurements, especially the ability to compare results from different measurement systems. Further problems are described in the next section.

3.1.1 PM_{10} and $\text{PM}_{2.5}$ measurements – current issues

Although most PM measurements in Europe are made using automated instruments, generally based either on variants of the Tapered Element Oscillating Microbalance (TEOM), on the attenuation of beta radiation by samples collected on a filter, or optical techniques, the reference method remains gravimetry. The automated methods need to show equivalence to the reference methods.

It has only become clear over recent years just how variable measurements of this mass on a filter can be, due to water content, semi-volatile particles and other artefacts. There are no reliable calibration mixtures of airborne PM, and in any case they could not replicate the complicated and highly variable mixture of substances found in practice. The definition of PM_{10} and $\text{PM}_{2.5}$ is therefore inherently method-dependent.

Ideally, any measurement method for PM_{10} and $\text{PM}_{2.5}$ must clearly address the following issues:

- 1 The allowable range of particle sizes;
- 2 The allowable range of water content in the PM – this is especially important for deliquescent components such as ammonium sulphate and sodium chloride, whose mass changes dramatically with water content;
- 3 The allowable losses of semi-volatile material, such as ammonium nitrate and some organic compounds. Losses can occur during sampling, and between sampling and weighing;
- 4 The allowable extent of chemical reactions during and after sampling, for example between reactive gases such as nitric acid and sulphur dioxide and the PM.

Because of the regulatory importance of gravimetric filter methods, other issues become inextricably linked to the operational definition of PM, notably:

- 1 The collection efficiency of the filter, at all relevant sizes, both in allowing particles to pass through and inefficiency caused by partial blockage;

- 2 Allowable chemical reactions between gaseous pollutants and the filter;
- 3 Allowable changes in filter mass between the pre-sampling and post-sampling weighing, due for example to water absorption or detachment of filter fibres;
- 4 Practical problems with measuring a small change in mass in a filter over a period of weeks, such as balance drift or static electrical effects.

Most of these issues have become more important over time, for the following reasons:

- 1 PM concentrations have fallen dramatically – by around a factor of 10 since the early 1960s (though they are still responsible for large numbers of premature deaths, and appear to have stabilised since around 2000) [1] – making all weighing errors more significant;
- 2 The emphasis has moved to lower size fractions, for example from PM_{10} to $PM_{2.5}$, so that smaller quantities are measured, again making all weighing errors more significant;
- 3 The composition of PM has changed from being dominated by combustion sources, notably domestic and industrial coal burning, to being a more variable mixture with major components of secondary material such as organics and nitrates, which are much more susceptible to the problems of water content and volatility.
- 4 The fact that the coarse fraction is dominated by crustal components, which are generally insoluble and non-volatile, compounds the previous two factors by making the $PM_{2.5}$ fraction proportionately more susceptible to humidity and temperature.

These problems are currently being addressed for European purposes through the European standardisation group CEN TC 264 WG 15. Standardisation of automatic methods is also being addressed. However, it should be noted that results of historical PM_{10} and $PM_{2.5}$ measurements need to be treated with some caution, and the problems will not be completely removed for the foreseeable future.

3.2 Number concentration

The main alternative to characterising airborne particle populations by mass concentration is by number concentration – the number of particles within a specified volume of air. In practice this is carried out either as a “total” number concentration, or as a number concentration in different size intervals.

3.2.1 “Total” number concentration

Particle number concentration is generally measured with Condensation Particle Counters (CPCs). These operate by passing the airstream through a supersaturated atmosphere containing, for example, butanol vapour, so that droplets of the vapour substance condense on the particles. These droplets, which are typically 10s of μm in size, can be detected optically, either individually by counting the flashes as they pass the detection system, or collectively, from the strength of a reflected signal, at higher concentrations.

As described in Section 1, the great majority of particles have a size less than 200 nm. CPCs therefore predominantly measure what can be called nanoparticles. Unlike PM_{10} and $PM_{2.5}$ measurements, where the upper size limit is important, there are so few particles in the coarse size range relative to the nanoparticle range that the effect of the upper size limit is negligible. In contrast, the lower size limit is important.

The size of the smallest particles to be detected by a CPC is determined by the nucleation conditions in the supersaturated vapour – for example the temperature and the condensing substance – and also the composition of the particles. A typical cut-off can be between 5 to 20 nm. Above the low size cut-off region, CPCs are generally very efficient at detecting particles, though there are small losses of particles within the instrument.

For ambient air measurements the low size cut-off curve has received little attention so far, and results have a low size cut-off set by the instrument being used, which may or may not have been accurately determined. Comparisons of results from different sources should therefore be treated with care.

3.2.2 Number concentration at different sizes

Particle size spectra are usually measured with Scanning Mobility Particle Sizers (SMPSs). These select a small subset of the particles according to their electrical mobility (related to their electric charge and their size), and measure the number of particles in the subset, typically with a CPC. The instrument scans through a range of electrical mobilities, and the results are converted to a size distribution. Some results from roadside and rural sites in the United Kingdom are shown in Figures 9 and 10. They show higher concentrations and smaller particles, associated with fresh vehicle emissions, at the roadside site compared with the rural site.

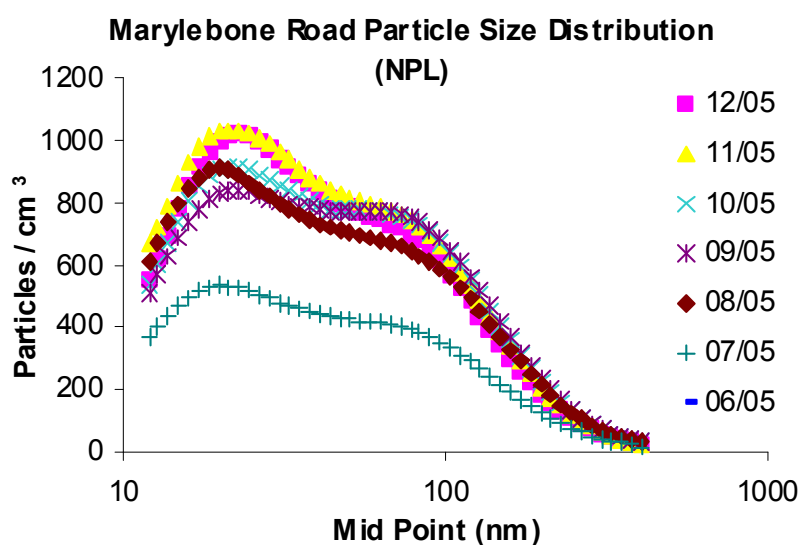


Figure 9: Particle size distributions from an SMPS at a UK roadside site, during 2005 as indicated.

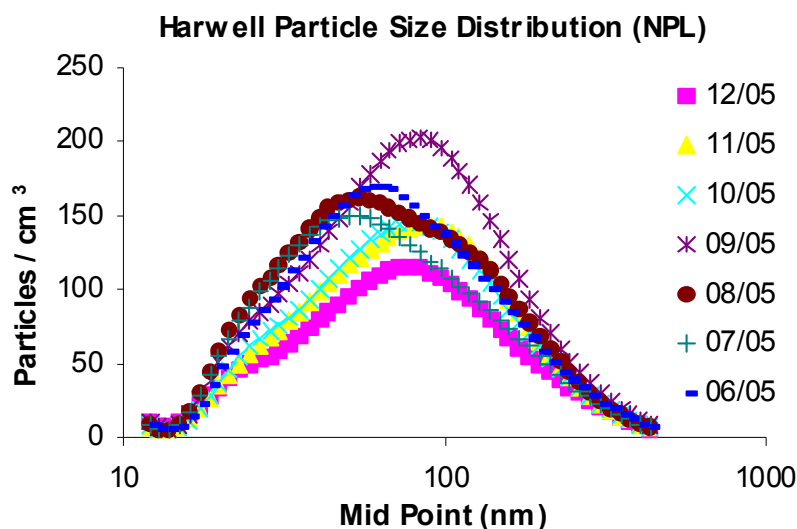


Figure 10: Particle size distributions from an SMPS at a UK rural site, during 2005 as indicated.

It would be very useful to use such results as the basis for studies of the health effects of a specific size range of particles. However, there are many factors, including the details of the software used to invert the data, and corrections for internal particle losses, that make comparability of data between different instruments problematic.

3.3 Mass concentration of chemical components

3.3.1 Major components

The recent Air Quality Directive [2] requires Member States to make measurements of the major components of PM_{2.5} at selected rural background sites. The specified components are the ions sulphate, nitrate, chloride, ammonium, sodium, potassium, calcium and magnesium, plus the components known as elemental carbon (EC) and organic carbon (OC).

The ionic components can be determined by ion chromatographic analysis of filter samples. Within the limitations of uncertainty relating to the material collected on the filter, such measurements can in principle be made more reliably than the total mass concentration measurements.

EC and OC are typically determined by thermal desorption and oxidation of material collected on filters, combined with an optically-determined correction for charring. The method is currently being standardised within Europe.

Because these measurements are a new regulatory requirement, and are focussed on rural background sites, existing measurements tend to have been made as part of limited campaigns, and have been of relatively little use to health effects studies.

3.3.2 Metals and polycyclic aromatic hydrocarbons (PAHs)

The chemical components of particles that have received most attention are the metals lead, arsenic, cadmium, and nickel, and PAHs, for which benzo(a)pyrene is taken as a tracer. Apart from lead, which is covered in [1], these feature in a separate Air Quality Directive [6]. The metals are typically measured using ICP-MS analysis of filter samples, while PAHs are measured by GC-MS analysis. Again, within the limitations of uncertainty relating to the material collected on the filter, such measurements can in principle be made more reliably than the total mass concentration measurements.

3.4 Other properties

3.4.1 Optical properties

One of the oldest quantitative measures of particle concentration is Black Smoke Index, which is determined by the darkness of material collected from a standard volume of air onto a filter of a standard size. The method, set out in ISO 9835, measures the darkness with a reflectometer, with a blank filter for comparison.

When initiated, the method provided a practical means for determining the quantity of coal and wood smoke, the dominant urban pollutants at the time. The method is not so well suited to the lower concentrations of more mixed pollutants in the present day. While quoted in units of $\mu\text{g}/\text{m}^3$, results do not represent the mass of the collected sample, or of the dark component, typically soot. Black Smoke Index results have been widely used for health effects studies because of the long period over which they have been made. Black Smoke has shown strong correlation with morbidity and mortality in epidemiological studies (eg [7]).

More modern optical methods measure what is termed Black Carbon by the absorption of samples on filters at specific wavelengths. These can give results (in $\mu\text{g}/\text{m}^3$) that are comparable with results for Elemental Carbon, with a much better time resolution.

3.4.2 Oxidative capacity

In terms of the properties of airborne particles causing health effects, one hypothesis is that the capacity of the particles to cause inflammation via the induction of oxidative stress is a key parameter. This capacity to cause oxidative stress appears to be related to the presence of oxidants or oxidant-generating components on the particle surface. The quantification of the oxidative capacity of particle samples is typically done by measures of the effects of particle samples on lung lining fluid in the laboratory [8].

4 Health effects of airborne particles

4.1 High level reports and reviews on particles in ambient air

4.1.1 World Health Organisation (WHO) reports

In 2001, WHO (Regional Office for Europe) agreed with the European Commission to provide the Clean Air For Europe (CAFE) programme of DG Environment with a systematic, periodic, scientifically independent review of the health aspects of air quality in Europe. Their reports therefore form an authoritative summary of health effects from airborne particles, and other air pollutants, from a European perspective. They assess the evidence from the two main strands of research: epidemiology (the study of patterns in data for pollutants, mortality and morbidity), and toxicology (the study of the toxic effects of specific substances on organisms or tissue).

The other major source of health effects studies and reviews is the USA. Given the European focus of this document, these will be discussed in less detail, in the next section, though it is important to note that many of the studies that have informed the WHO reports originate in the USA.

The timing of the WHO reports has been linked to the revision of the 1996-2002 EU Air Quality Directives, with their conclusions directly influencing the 2008 Air Quality Directive. To some extent this has limited the scope of the reports, as they put strong emphasis on those metrics that were expected to feature in the legislation, namely PM₁₀ and PM_{2.5}.

The central document is the 2003 report *Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide* [9]. This updated the 2000 guidelines given in *WHO Air Quality Guidelines for Europe*, Second edition [10]. To quote the main conclusion relating to airborne particles from the 2003 report:

The WG adopted a recommendation to use fine particulate matter, (PM_{2.5}), as the indicator for health effects induced by particulate pollution such as increased risk of mortality in Europe, to supplement the commonly used PM₁₀ (which includes fine and coarse particles).

The conclusion was therefore to acknowledge the importance of evidence, primarily from the USA, that the fine fraction was most strongly associated with health effects, but without concluding that the coarse fraction was harmless.

Regarding the characteristics of the particles causing the health effects, there are no firm conclusions beyond the identification of the fine fraction. To quote some relevant passages:

Amongst the characteristics found to be contributing to toxicity in epidemiological and controlled exposure studies are metal content, presence of PAHs, other organic components, endotoxin and both small (< 2.5 µm) and extremely small size (< 100 nm).

Possibly relevant chemical characteristics include the content of transition metals, crustal material, secondary components such as sulphates and nitrates,

polycyclic aromatic hydrocarbons and carbonaceous material, reflecting the various sources that contribute to PM in the atmosphere.

In many time series and in some of the cohort and cross sectional studies, sulphates are found to predict adverse effects well. It has been suggested that this may be related to interactions between sulphate and iron in particles but it should be pointed out that in animal experiments, it has generally not been possible to find deleterious effects of sulphate aerosols even at concentrations much higher than ambient.

More research is needed to establish the possible links between ultrafine (< 100 nm) PM sources, exposures and health more accurately and precisely.

The 2003 report has been supplemented by several other reports:

Meta-analysis of time-series and panel studies of Particulate Matter (PM) and Ozone (O₃) (2004) [11].

Health Aspects of Air Pollution – answers to follow-up questions from CAFÉ (2004) [12].

Health effects of transport-related air pollution (2005) [13]

Health relevance of particulate matter from various sources (2007) [14].

The current state of uncertainty regarding the causes of health effects from airborne particles can be gauged from the conclusions of the last of these reports, which include:

Research in this area should analyse a wide range of PM sources beyond road traffic or heat and power generation, such as local and regional wood burning or desert dust;

Air quality monitoring must widen component speciation and allow better source apportionment;

Easy-to-operate, low-cost instrumentation for PM monitoring, especially for estimating longterm exposures, should be developed;

Research should explore the role of various characteristics of ultrafine, fine and coarse thoracic particles that might be responsible for health effects.

4.1.2 The extent of health effects from particles in Europe

Aside from the question of the specific cause of adverse health effects from airborne particles, there is a separate question about the scale of these effects. This was addressed in the report *CAFE Cost Benefit Analysis: Baseline Analysis 2000 to 2020* (2005) [15], which was produced as part of the evidence to inform the revision of the Air Quality Directives. This identified airborne particles as having by far the highest impact on human health across Europe, with ground level ozone the second most important pollutant in this respect. The figures for Europe as a whole are presented in Table 4, which estimates that there were 347,900 premature deaths from airborne particles in 2000, and 21,400 from ozone.

Table 5. Implementing current EU legislation: Estimated annual health impacts due to air pollution in 2000 and in 2020 in EU25, plus the change (benefits) from current legislation (2000 to 2020)

End point	End point output	Function Group		Baseline in 2000	Current legislation in 2020 (including Climate Policy)	Difference from 2000 to 2020
Acute Mortality (All ages)	Premature deaths	Core	O ₃	21,400	20,800	600
Respiratory Hospital Admissions (65yr +)	Cases	Core	O ₃	14,000	20,100	-6,100
Minor Restricted Activity Days (MRADs 15-64yr)	Days	Core	O ₃	53,913,600	42,415,500	11,498,100
Respiratory medication use (children 5-14yr)	Days	Core	O ₃	21,355,900	12,925,900	8,430,000
Respiratory medication use (adults 20yr +)	Days	Core	O ₃	8,833,600	8,171,700	661,900
Cough and LRS (children 0-14yr)	Days	Core	O ₃	108,076,600	65,278,600	42,798,000
Chronic Mortality *	Life years lost	Core	PM	3,618,700	2,467,300	1,151,400
Chronic Mortality *	Premature deaths	Core	PM	347,900	271,600	76,300
Infant Mortality (0-1yr)	Premature deaths	Core	PM	677	352	325
Chronic Bronchitis (27yr +)	Cases	Core	PM	163,800	128,100	35,700
Respiratory Hospital Admissions (All ages)	Cases	Core	PM	62,000	42,300	19,700
Cardiac Hospital Admissions (All ages)	Cases	Core	PM	38,300	26,100	12,200
Restricted Activity Days (RADs 15-64yr)	Days	Core	PM	347,687,000	221,999,100	125,687,900
Respiratory medication use (children 5-14yr)	Days	Core	PM	4,218,500	1,987,700	2,230,800
Respiratory medication use (adults 20yr +)	Days	Core	PM	27,741,700	20,879,800	6,861,900
LRS symptom days (children 5-14yr)	Days	Core	PM	192,756,400	88,852,300	103,904,100
LRS in adults (15yr +) with chronic symptoms	Days	Core	PM	285,345,000	207,562,100	77,782,900

*Note two alternative metrics are used for the presentation of chronic mortality from PM. Firstly in terms of years of life lost and secondly in terms of numbers of premature deaths. These are not additive.

Table 4: taken from reference 15.

The premature deaths in 2000 were estimated to be distributed geographically as in Figure 11.

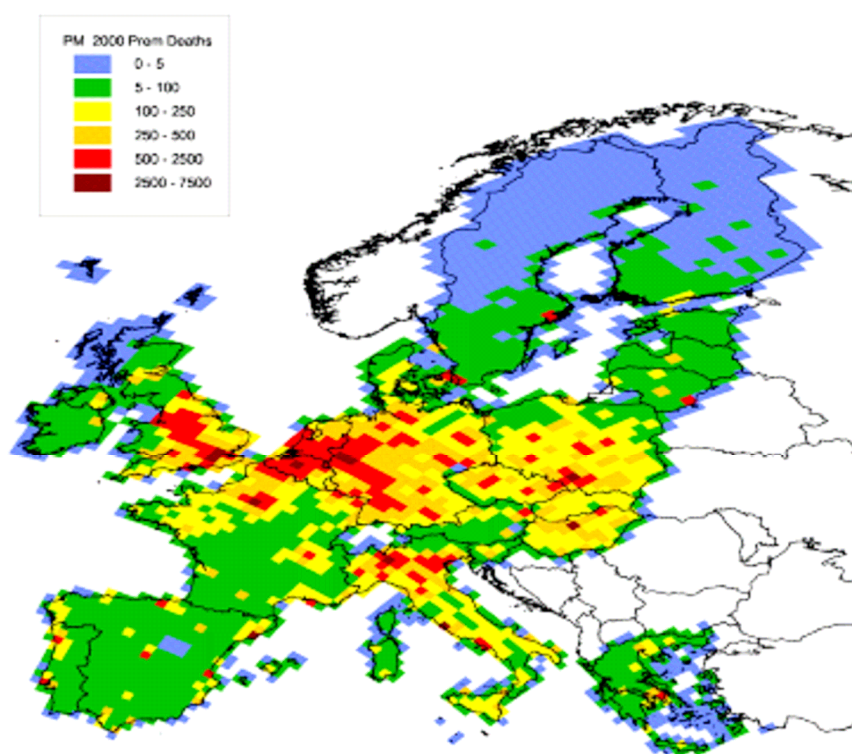


Figure 11: Premature deaths from PM across the EU in 2000, taken from [15].

4.1.3 US Environmental Protection Agency

The main review from the US Environmental Protection Agency is Air Quality Criteria for Particulate Matter, 2004 [16], which led to a reduction in the US limit value for PM_{2.5} in 2006. This large document is a major resource on all aspects of airborne particles. Selected conclusions relating to health effects were:

From epidemiology:

Thoracic Particles. An extensive body of epidemiology evidence, confirming earlier reported associations between short- and long-term exposures (inferred from stationary air monitor measures) to ambient thoracic particles (typically indexed by PM₁₀) and mortality/morbidity effects, supports the general conclusion that ambient thoracic particles, acting alone and/or in combination with gaseous co-pollutants, are likely causally related to various human health endpoints.

Fine-fraction particles. A growing body of epidemiologic evidence both (a) confirms associations between short- and long-term ambient exposures (inferred from stationary air monitor measures) to fine-fraction particles (generally indexed by PM_{2.5}) and various mortality or morbidity endpoint effects and (b) supports the general conclusion that PM_{2.5} (or one or more PM_{2.5} components), acting alone and/or in combination with gaseous co-pollutants, are likely causally related to observed ambient fine particle associated health effects.

Coarse-fraction particles. A much more limited body of evidence is suggestive of associations between short-term (but not long-term) exposures (inferred from stationary air monitor measures) to ambient coarse-fraction thoracic particles (generally indexed 10-2.5) and various mortality and morbidity effects observed at times in some locations. This suggests that PM_{10-2.5}, or some constituent component(s) of PM_{10-2.5}, may contribute under some circumstances to increased human health risks.

Co-pollutant confounding and effects modification. Much progress has been made in sorting out contributions of ambient PM₁₀ and its components to observed health effects relative to other co-pollutants; and, despite continuing uncertainties, the evidence overall tends to support the above conclusions that ambient PM₁₀ and PM_{2.5} are most clearly associated with mortality/morbidity effects, acting either alone or in combination with other covarying gaseous pollutants, with more limited support with regard to PM_{10-2.5}.

From toxicology:

To date, experimental toxicology studies have provided some intriguing, but limited, evidence for ambient PM mixes or specific PM components potentially being responsible for reported health effects of ambient PM.

There is growing toxicological evidence that, analogously to several other types of PM (silica, CB, road dust, etc.), diesel PM may exacerbate allergic responses to inhaled antigens.

Studies of various types of ultrafine particles have demonstrated a significantly greater inflammatory response than that seen with fine particles of the same chemical composition at similar mass doses.

4.2 Selected topics

It must be understood that very large numbers of scientific papers relating to the health effects of airborne particles are published in journals such as Toxicology, Epidemiology, Occupational and Environmental Medicine, Environmental Health Perspectives, Inhalation Toxicology, American Journal of Respiratory and Critical Care Medicine, Thorax, New England Journal of Medicine, Journal of Epidemiology and Community Health, and American Journal of Epidemiology (to give a few specific examples). It is clearly not feasible in this document to

summarise recent research, and indeed this is the job of the authoritative reviews described above.

The sections below are inevitably highly selective. The aim is to provide some useful additional information.

4.2.1 The Harvard Six Cities study

Perhaps the most influential single study into the effects of airborne particles on human health, the Harvard Six Cities Study was published in 1993 [17]. This was a prospective cohort study with data from a 14-to-16-year mortality follow-up of 8111 adults in six U.S. cities with varying levels of pollution, with care taken to control for cigarette smoking and other health risks.

One of the central results was the much higher correlation between health effects and fine particles compared with health effects and total particles, as shown in Figure 12. The cities, indicated by their initials, were Watertown, Massachusetts; Harriman, Tennessee; St. Louis (L); Steubenville, Ohio; Portage, Wisconsin; and Topeka, Kansas.

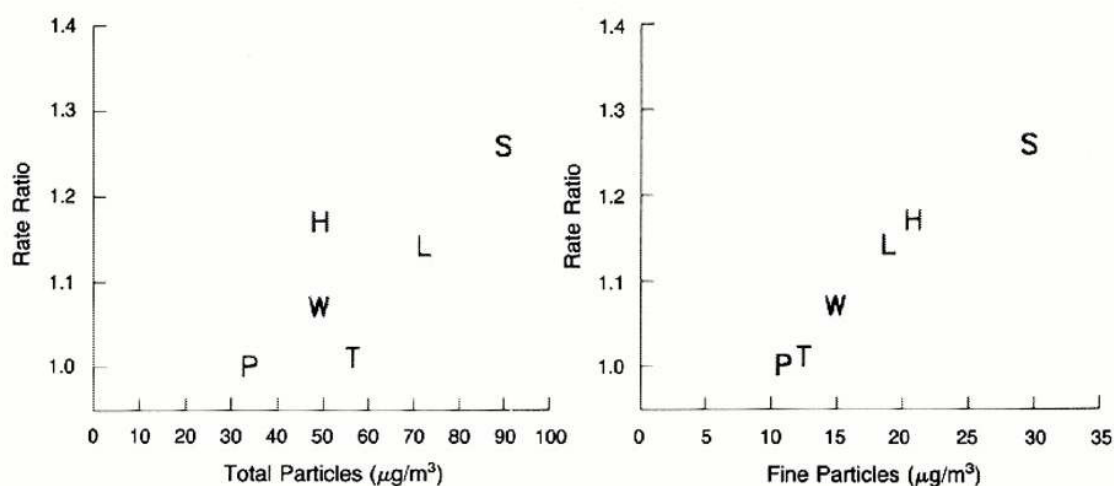


Figure 12 : Correlations between health effects and particle concentrations, taken from [17].

More recent reanalysis of the data by the Health Effects Institute in 2003 [18] essentially confirmed the original findings.

4.2.2 APHEA

The project APHEA (Air Pollution and Health, A European Approach), and its successor APHEA 2, collated and analysed much of the particle health effects information for Europe eg [19], and this was used in the process of revising the Air Quality Directive.

4.2.3 Ultrafine particles (or nanoparticles)

A potentially important role for ultrafine particles in causing health effects was highlighted in 1995 [20]. As mentioned above, the toxicological effects of such small (<100nm) particles can be much greater than the effects of the same mass of larger particles [16].

A review of some aspects of ultrafine particles and their effects on health was published in 2005 [21]. In practice this is a very active area of study, spawning the new discipline of nanotoxicology, and it would be premature to form conclusions [22].

4.2.4 Coarse particles

The recent regulatory emphasis in both Europe and the USA on fine particles (PM_{2.5}) has to some extent left the coarse fraction less well evaluated. The evidence of health effects from the coarse fraction was reviewed in 2005 [23].

To quote from this review:

Time series studies relating ambient PM to mortality have in some places provided evidence of an independent effect of coarse PM on daily mortality, but in most urban areas, the evidence is stronger for fine particles. The few long-term studies of effects of coarse PM on survival do not provide any evidence of association.

In studies of chronic obstructive pulmonary disease, asthma and respiratory admissions, coarse PM has a stronger or as strong short-term effect as fine PM, suggesting that coarse PM may lead to adverse responses in the lungs triggering processes leading to hospital admissions. There is also support for an association between coarse PM and cardiovascular admissions.

It is concluded that special consideration should be given to studying and regulating coarse particles separately from fine particles.

It is fair to conclude that the characteristics of airborne particles, which may relate to size, morphology, chemical composition, chemical activity, or some combination of these, that determine the extent of their adverse health effects on people, have not yet been reliably determined, and that any techniques that can help to characterize airborne particles will be useful tools to help clarify the situation.

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