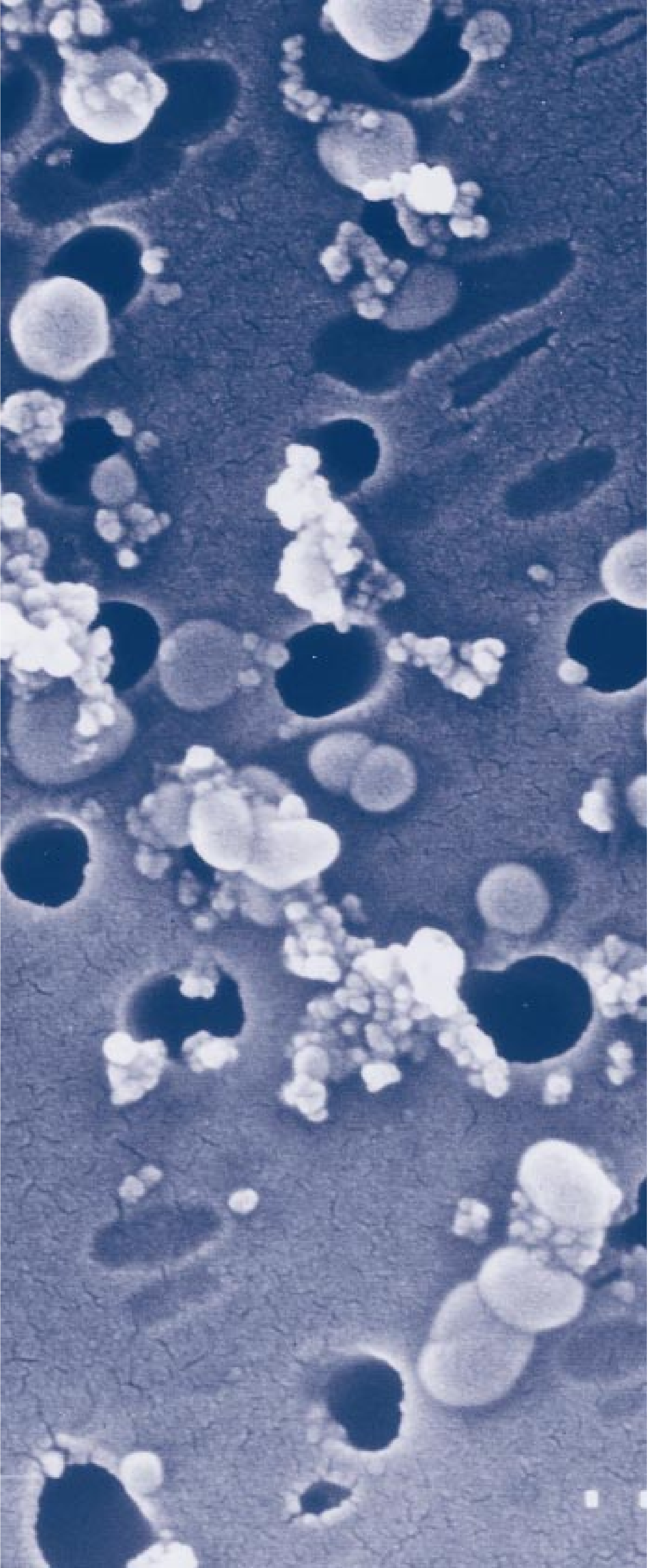

Airborne Particulate Matter in the United Kingdom

May 1996

Third Report of the
Quality of Urban Air Review Group

Prepared at the request of the
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Cover Picture: Airborne Particles Collected on the Surface of a Nuclepore Filter from the Atmosphere of Birmingham

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The authors accept responsibility for the contents of this report but the views are their own and not necessarily those of the organisations to which they belong or the Department of the Environment

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Executive Summary

Airborne particulate matter is a very diverse material in terms of its physical and chemical properties and there are many sources which contribute to atmospheric concentrations. This report, the Third Report of the Quality of Urban Air Review Group, reviews knowledge of the sources, chemical composition and physical properties and concentrations of airborne particles and examines the implications for control of particulate matter in UK urban air.

Airborne particles are typically very small; they range in size from a few nanometres in diameter to 100 or more micrometres*. Whilst particles from throughout this range can be found in the atmosphere, those capable of remaining airborne for long periods (typically 10 days or so), are in the more limited size range of approximately 0.1-2 micrometres diameter. The size fraction measured by the UK Automatic Urban Network includes particles up to 10 micrometres (termed PM_{10}). The Report reviews the methods available for measuring airborne particulate matter and highlights the performance characteristics of various common instruments.

Airborne suspended particulate matter may be either primary or secondary in its origins. Primary particles are those directly emitted to the atmosphere from sources such as road traffic, coal burning, industry, windblown soil and dust and sea spray. On the other hand, secondary particles are particles formed within the atmosphere by chemical reaction or condensation of gases, and the major contributors are sulphate and nitrate salts formed from the oxidation of sulphur dioxide and nitrogen oxides respectively. Emissions inventories are available for primary particulate matter which indicate that nationally the major sources are road transport (25%), non-combustion processes such as construction, mining and quarrying and industrial processes (24%), industrial combustion plants and processes with combustion (17%), commercial, institutional and residential combustion plants (16%) and public power generation (15%). Industrial sources may thus lead to locally elevated concentrations of PM_{10}. Domestic coal burning in some areas of the UK, for example Belfast, can also lead to elevated levels. Within urban areas generally, however, the influence of road traffic is far more marked and in Greater London it is estimated that 86% of PM_{10} emissions in 1990 arose from this source. The contribution of secondary particles is far more uniform as these are formed relatively slowly in the atmosphere and have a long atmospheric lifetime. Nonetheless, there is a distinct gradient in concentrations with the highest in the south-east of the UK, decreasing progressively to the north and west. Recent data show concentrations of secondary particles some 10% higher in the spring and summer months of the year than the annual average.

For many years measurements of particles in the UK atmosphere have been carried out using the black smoke method. This depends upon the blackness rather than the weight of particles. Originally, this was designed to measure airborne particles derived from the burning of coal, but nowadays in most urban areas the measurements reflect primarily emissions from diesel vehicles. More recently, automatic measurements of PM_{10} have been made and data from the UK Automatic Urban Network show uniformity of annual average concentrations across the major UK urban areas, with mean concentrations within the range of 20-30 micrograms per cubic metre. Exceptional behaviour has been observed in Belfast where coal burning is still a major source of airborne particles, and for a time in Cardiff when construction activity adjacent to the sampling site influenced the measurements. Examination of the highest daily mean concentrations shows a seasonal pattern with the highest values generally occurring in the winter months with variations between urban areas much clearer than for the annual average concentration. There are relatively few data for rural measurement of PM_{10}, but it appears that concentrations are of the order of 10-15 micrograms per cubic metre, reflecting mainly secondary particles.

Receptor modelling techniques based upon an analysis of measurements of airborne particles and their chemical components have been used to identify the major contributors to PM_{10} in urban air. The results indicate that exhaust emissions from road traffic together with secondary particles dominate the $PM_{2.5}$ (small particle) fraction which comprises the major part of elevated PM_{10} concentrations and hence is potentially more important in relation to health impacts. The sources of coarse particles, in the 2.5-10 micrometre range, are less clearly defined, but resuspended street dusts, windblown soils and sea spray particles are major contributors. In the winter months

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* 1 nanometre is one millionth of a millimetre; 1 micrometre is one thousandth of a millimetre.

episodes of high PM_{10} are associated almost wholly with raised concentrations of $PM_{2.5}$ arising from vehicle exhaust emissions. In summer, the contribution of secondary particles during photochemical pollution episodes is also important. Road traffic contributes to secondary particle formation through emissions of NO_x. Emissions inventories do not currently give a complete breakdown of the sources of particulate matter in UK urban air as they cannot account for secondary particles, and estimates of emissions from diffuse and natural sources such as dust suspended from road surfaces by wind and traffic-induced turbulence are subject to very great uncertainties.

There are currently many exceedences of the EPAQS recommended limit of 50 micrograms per cubic metre as a running 24 hour average concentration. For example, in Central London between 1992 and 1994 this value was exceeded on 75 days measured from midnight to midnight, or 139 days when measured as a 24-hour running mean in accordance with the EPAQS recommendation. Control of PM_{10} concentrations to within the limit recommended by EPAQS will require major controls on the sources of emission. In winter, our analysis shows that far the major contributor to episodes of high PM_{10} concentration is exhaust emission from road transport. A reduction of about two thirds in emissions from this source would lead to achievement of the air quality standard at background sites in most UK urban areas, but control of roadside concentrations and pollution episodes to meet the EPAQS recommendation would require further emission reductions. For example, to have limited 24-hour average PM_{10} to below 50 $\mu g/m^3$ in the December 1991 pollution episode in London is estimated to require a reduction of over 80% in road traffic exhaust emissions. Current projections indicate a cut in emissions of about 52% by 2010. In summer, secondary sulphate and nitrate particles formed from atmospheric oxidation of sulphur and nitrogen oxides appear to be the primary cause of episodes of high PM_{10} concentration, although in summer the contribution of coarse particles, largely resuspended surface dusts, is also important. Numerical model predictions indicate that agreed controls on emission of sulphur and nitrogen oxides across Western Europe will deliver an improvement of about 40% in average concentrations of secondary particles across the UK by the year 2010. This alone is unlikely to be sufficient to bring summer concentrations in line with the EPAQS recommendation.

Our analyses clearly indicate the need for tighter controls on the sources of PM_{10} to achieve the EPAQS standard throughout the UK. In some areas improved controls on industry and a reduction in emissions from the burning of solid fuels for home heating may be required. However, for the majority of UK urban areas the key sources requiring control if air quality is to meet the standards recommended by EPAQS are twofold. The first is road traffic, and our Second Report pointed out the particularly important contribution of diesel emissions in regards of atmospheric particulate matter. The second is that of secondary particles formed in the atmosphere from emissions of sulphur and nitrogen oxides. These are formed from Europe-wide emissions rather than solely those from the UK, and hence international agreements for SO_x/NO_x control beyond those already in place will also be needed.

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1 Introduction

In its First Report (QUARG, 1993a) this Review Group sought to summarise the present state of knowledge with regard to the urban air pollution climate of the United Kingdom. Concern was expressed that a number of pollutants exceed present health-based standards and guidelines. It was also noted that increasingly, as other sources come under better control, the relative importance of motor vehicle traffic as a source of air pollution in our towns and cities has increased. Comparing national and urban inventories of pollutant emissions, there are major divergences attributable to the greater impact of road traffic in urban areas. A tentative look into the future revealed that toughening standards on vehicle emissions will lead to significant improvements in air quality over the next five or ten years, but that unless such emission standards were tightened yet further, an increase in traffic growth could negate the benefits obtained from lower pollutant emissions per vehicle, and that for many pollutants, concentrations might once again start to increase after about 2005.

Having highlighted the important role of road traffic in influencing urban air quality, it was natural that our Second Report (QUARG, 1993b) should deal with a major aspect of this question. The Report reviewed the impact of diesel vehicle emissions on urban air quality and highlighted the fact that with the advent of three-way catalytic converters on new petrol cars, the impact of diesel emissions, at that time mostly from Heavy Duty Vehicles (trucks and buses), on urban air quality would become more marked. A further contribution to this trend was also arising from a substantially increased market penetration of diesel cars which had until 1991 comprised only about 5-6% of the new car market, but increased rapidly to take about 25% of the market at the end of 1993. The report highlighted the very large contribution which diesel emissions make to urban concentrations of particulate matter in general, black smoke in particular, and of nitrogen oxides. Based upon an evaluation of the relative importance of the various vehicle-emitted pollutants and of future trends in emissions, the Review Group expressed concern over the impact of particulate matter and nitrogen oxides from diesels on urban air quality and recommended against an increase in the number of diesel vehicles on our roads unless problems with these two pollutants are effectively addressed.

Since the publication of our Second Report, considerable new information has emerged. A detailed evaluation of the December 1991 pollution episode in London has revealed an increase of about 10% in mortality during the week of the episode compared with the same period in earlier years (Anderson et al, 1995). Statistically significant increases in some illnesses were also established. A careful analysis of the data led to the conclusion that the most probable cause of the adverse health effects was air pollution, and it appears that the deadly smogs of the 1950’s and 1960’s have not been wholly banished. The 1991 episode appears to be a more modern manifestation of those serious pollution incidents and has in common with them the greatly elevated levels of black smoke particles, but differs in that concentrations of sulphur dioxide were very much lower in 1991, but oxides of nitrogen were probably considerably elevated over concentrations in the 1950's, before routine measurements of nitrogen oxides were made.

The epidemiological evidence for the adverse health effects of airborne particles has also strengthened greatly since the publication of our Second Report. There have been further publications of time series studies in which day-to-day changes in mortality and illness are shown to be related to concentrations of airborne particulate matter. Additionally, two major cross-sectional studies in which mortality rates in different cities have been shown to relate to their air pollution have been published. The Harvard Six Cities Study (Dockery et al, 1993) examined mortality amongst 8,000 known individuals over a period of some 15 years and after controlling for other risk factors such as smoking, excess body weight and socio-economic class, showed a strong relationship between mortality and the concentration of fine particulate matter in the atmosphere. The more recent study based upon the American Cancer Society database of over half a million people used data on fine particulate matter from some 50 urban areas as well as particulate sulphate data from 151 urban areas, showing a clear relationship between mortality and concentrations of the air pollutant (Pope et al, 1995).

As a reaction to the increasing weight of evidence on the adverse health effects of airborne particles, other UK advisory panels and committees have also been active. The Expert Panel on Air Quality Standards has recently concluded its deliberations upon airborne particulate matter and has recommended a standard. In parallel with this exercise, the Department of Health's Committee on the Medical Effects of Air Pollution appointed a Sub-Committee on Particulate Matter which has published a detailed report on non-biological particles and health. These reports provide valuable advice upon the health risks of particulate matter which will form part of the information needed by Government to formulate policy.

The Quality of Urban Air Review Group also has a role to play in providing advice on particulate matter and this, our Third Report, seeks to provide information from our perspective as air pollution scientists. Current research suggests that the health impact of airborne particles is dependent upon their size, but apparently not upon their chemical composition. One hypothesis on the biological mechanism of health injury due to airborne particles implies that the number of particles to which the individual is exposed is more important than their mass (Seaton et al, 1995). In this Report we seek to review knowledge on both the chemistry and physics of airborne particles. We provide information on the measured sizes of particulate matter in the UK atmosphere as well as on the chemical composition, which may yet prove to be significant in the toxicity, but notwithstanding, is a very valuable indicator of the source of the particles.

Any control strategy for airborne particulate matter must be based upon a firm understanding of the origins of those particles and the factors which influence their concentrations in the atmosphere. This report seeks to review the current state of knowledge on these issues. For example, it is clear that airborne particulate matter may be both primary, ie emitted as such into the atmosphere, or secondary, ie formed in the atmosphere from chemical reactions of gaseous precursors such as sulphur and nitrogen oxides. The two kinds of particulate matter show different seasonal patterns and a different dependence upon the control of sources. Here we seek to review the limited knowledge available on the partition between primary and secondary sources, and upon the contributors to the primary particulate matter in the atmosphere.

The review and analysis included in this Report reveals the considerable diversity in the sources of particulate matter and the many factors influencing its atmospheric behaviour. In this context, particulate matter is certainly the most complex of the common air pollutants to understand and may ultimately prove one of the most difficult to control because of its multiplicity of sources. However, by targeting major sources of primary emissions such as road traffic, as well as sources of the sulphur oxide and nitrogen oxide precursors of secondary aerosol, it should be feasible to make progress over the coming few years. Refined and updated projections of future emissions are included in this Report.

1.1 SOURCES OF AIRBORNE PARTICULATE MATTER

At this point in the Report it is appropriate to give a very brief summary of the sources of airborne particles. Those which are relevant will be amplified further in the Report. On a global scale a number of natural sources such as volcanic emission of particles, forest and brush fires and ingress of extra-terrestrial particles into the atmosphere may be significant. In the context of the United Kingdom, and particularly in relation to urban areas, these sources are dwarfed by particles arising from human activity and will not be considered further.

Suspension of Soil Dust

The action of the wind on dry loose soil surfaces leads to particles blowing into the air. This is most obviously seen in association with sand and dust storms common during windy conditions in the world's deserts. These processes do, however, extend to other regions of the globe, although their magnitude is obviously reduced where soils are moist and have vegetation cover. It is estimated that suspension of surface soils causes the introduction of 150 million tonnes of dust per year to the Northern Hemisphere atmosphere and around double this if the Sahara Desert is included. This leads to an atmospheric burden of dust in the Northern Hemisphere, (excluding the Sahara plume) of 3 million tonnes on average. The presence of such particles in the UK atmosphere is manifested by the accumulation of dust on surfaces such as motor cars during dry weather periods. Much enhanced deposition is occasionally seen when the atmosphere carries dust from the Sahara Desert regions. Such particles are generally rather coarse (ie large in size) and frequently have only a limited atmospheric lifetime and range, although their transport from North Africa to the UK shows that this is not always the case.

Factors favouring the suspension of soil dust particles into the atmosphere are an exposed dry surface of fine soil and a strong windspeed. In towns and cities the areas of exposed soil, particularly in town centres, are rather small. However, there are considerable quantities of dusts on road and pavement surfaces which arise from ingress of soil on vehicle tyres and from the atmosphere, the erosion of the road surface itself and degradation of parts of the vehicle, especially the tyres. Because these particles lie on a surface which readily dries, and are subject to atmospheric turbulence induced by passing vehicles, this provides a ready source of particles for resuspension into the atmosphere. The amounts of dust resuspended in this process are extremely difficult to predict or measure as they depend critically upon factors such as the dust loading of the surface, the preceding dry period and the speed of moving traffic. However, the size distribution and chemical composition of particles in the urban atmosphere give a clear indication that this source contributes significantly to the airborne particle loading of our cities.

Seasalt

Breaking waves on the sea cause the ejection of many tiny droplets of seawater into the atmosphere. These droplets dry by evaporation leaving seasalt particles suspended in the air. Whilst these particles are, in the main, rather coarse in size, a minor part of the mass is in particles small enough to have an appreciable atmospheric lifetime, and all parts of the UK are influenced to some extent by particles of seasalt. Clearly, coastal areas are the most affected, but seasalt is measurable even at the most inland of UK locations. In winter months, identification of this source by measurement of the chemical composition of airborne particles is complicated by the use of salt for de-icing the roads. Most road de-icing salt has a chemical composition almost identical to that of seasalt and the two are effectively indistinguishable. Vehicles travelling at high speed on the motorway in wet conditions raise very visible plumes of spray which contain salt if the road has been treated with de-icing salt. Although the process is less visible, it occurs also on urban roads at lower traffic speeds.

Anthropogenic Primary Particles

All combustion and metallurgical processes and many other industrial operations lead to the emission of particles into the atmosphere. If these particles are directly emitted from a source, they are termed primary. The largest individual contributor of particles is combustion processes, although the mode of formation and chemical composition of the particles varies greatly from one source to another. Thus, in the case of coal combustion, the major part of the particle emissions arises from so-called fly-ash, which is fine particles of mineral material contained in the coal. In the case of emissions from diesel vehicles, the particles comprise largely elemental and organic carbon with some sulphate and water. Fuel is introduced into the combustion chamber of the engine as a spray of fine droplets, each of which leaves a tiny residual particle of unburned and pyrolysed fuel and oxidised sulphur which is emitted from the exhaust. Combustion of other more volatile carbon-containing fuels can lead to formation of carbon-based particles through combination of carbon atoms within the combustion zone. High temperature metallurgical processes and refuse incineration cause the formation of fine metal-rich particles by the condensation of cooling vapours. Despite the best efforts of arrestment plants, a small proportion of such particles inevitably enter the atmosphere. The emissions of anthropogenic primary particles are those most easily quantified and inventories of emission are available which will be elaborated upon later in this report.

Many other industries and processes also lead to emissions of primary particles. These include, for example, mining, quarrying, construction and demolition.

Anthropogenic Secondary Particles

The term secondary particles is used to describe those particles that are formed within the atmosphere, mostly from the chemical oxidation of atmospheric gases. The most prevalent secondary particles are sulphates formed from the oxidation of sulphur dioxide. The first product of this oxidation process is a mist of sulphuric acid droplets, although there is generally ample ammonia available in the UK atmosphere to neutralise this first to ammonium bisulphate and subsequently to ammonium sulphate. This compound is one of the most abundant substances in UK air.

Nitrogen dioxide may also be oxidised in the atmosphere to form nitric acid. The latter is more volatile than sulphuric acid and exists in the atmosphere in the gas phase, but when reacted with ammonia can form particles of ammonium nitrate. It can also react with seasalt particles to form sodium nitrate. Another less abundant form of secondary particles comprises ammonium chloride formed from the reaction of ammonia with hydrochloric acid gas emitted from combustion of coal and municipal incineration.

Chemical reactions of hydrocarbons within the atmosphere can also lead to the production of involatile or semi-volatile products which contribute to the loading of atmospheric particles. The composition of such particles and the chemistry leading to their formation has been studied in the context of pollution in Southern California, but there has been no research on the matter in the UK, and whilst it is likely that secondary organic materials are a component of particles in the UK atmosphere, there is currently no data upon the concentrations or composition.

Biological Particles

It has long been known that the atmosphere acts as a medium for transport of a variety of biological particles. The sizes of such particles cover a very wide range. Vegetation canopies are a major source of natural biological particles such as those derived from fungal, bacterial and viral plant pathogens as well as pollen grains derived from the flowers of wind-pollinated plants. There are well established networks for sampling, counting and identifying airborne pollens and spores in the UK atmosphere. Information on bacteria and viruses is much more scarce, generally being related to investigations of specific problems. However, the recent development of DNA-based techniques in molecular biology offers the opportunity for more extensive work in this field.

Airborne biological particles can cause disease. The effects produced are dependent on the nature of the particles: viral, bacterial, fungal or pollen. While such effects are of important health significance they are not a facet of urban air pollution specifically and are outside the remit of this Report.

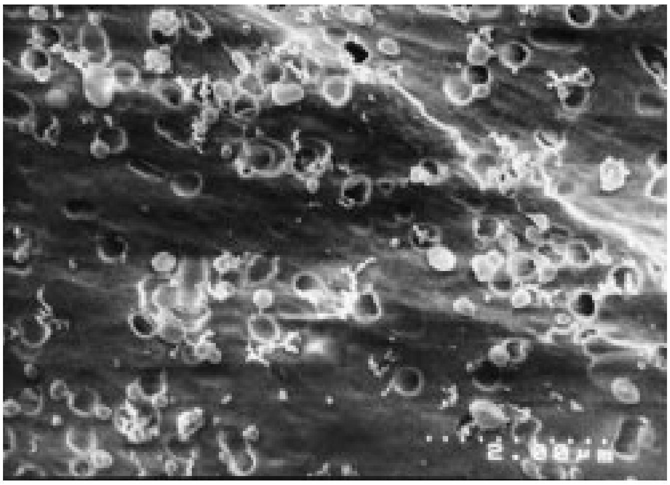
1.2 SIZES AND SHAPES OF AIRBORNE PARTICLES

Airborne particles cover a very wide size range from a few nanometres (billionths of a metre) to tens of micrometres (millionths of a metre). The recently published EPAQS recommendation relates to PM_{10}, or particles passing an inlet of defined characteristics with a 50% sampling efficiency at 10 micrometres (µm) aerodynamic diameter. Thus, to a good approximation, PM_{10} is particulate matter smaller than 10 µm diameter, and usually comprises the majority of airborne particle mass. Particles outside of this size range are relatively very large in size and have little impact on health. Within the PM_{10} size range, particles of less than 2.5 µm aerodynamic diameter (known as $PM_{2.5}$) are normally described as fine, whilst the 2.5 to 10 µm fraction is termed coarse. The fine particles are capable of reaching the deepest part of the lung, whilst coarse particles generally deposit in the upper airways. As a rough generalisation, particles generated from combustion and condensation of vapours are mostly in the fine fraction, whilst particles from mechanical break-up of solids and liquids are coarse.

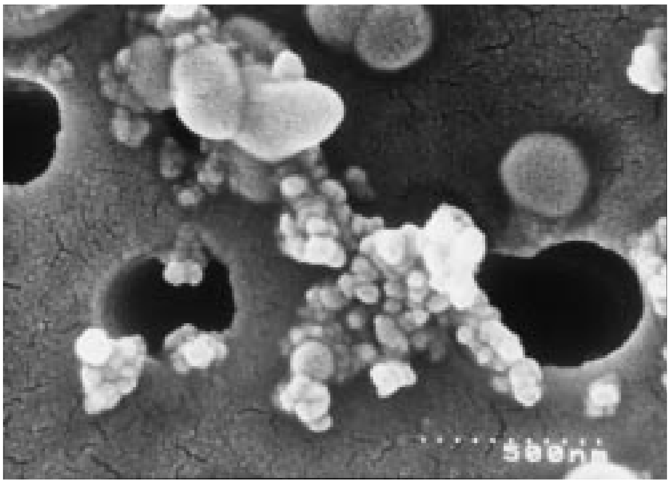
The physical form of PM_{10} may be assessed by electron microscopy. Some examples appear in

Figure 1.1 Airborne Particles Collected on the Surface of a Nuclepore Filter from the Atmosphere of Birmingham. The Dark Circles are Pores in the Filter, about 0.4 micrometres in Diameter.

(a) Mixed small particles. The branched chain structures are probably vehicle-generated particles.



(b) Close-up of a cluster formed from coagulation of many small particles, each about 50 nanometres in diameter.



(c) Two very large particles, about 5 micrometres in diameter. One (on the left) appears to be a layered mineral, whilst the other is a massive cluster of tiny particles.

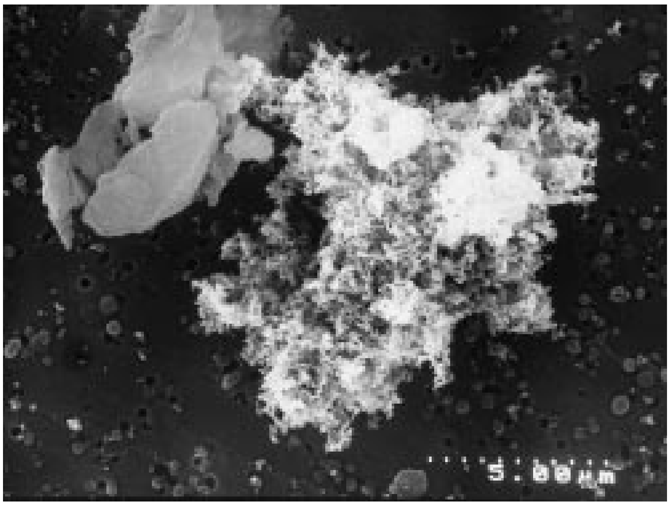


Figure 1.1. This exemplifies the wide variety of sizes and shapes of particles typically encountered in the atmosphere.

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2 Properties of Airborne Particulate Material

2.1 INTRODUCTION

Simple physical processes and properties profoundly influence the behaviour of atmospheric particles, and their effects on our health and environment. The air near the ground contains a variable mixture of diverse particles, some solid and some partly or wholly liquid, including many of the pollutants of current concern. Although the properties of each particle differ according to its size, shape and composition, the effect of particle size is strongly dominant.

The purpose of this Chapter is to provide a brief overview of the properties of aerosol particles that are of major importance. The persistence in the air affects the atmospheric concentration and the distance travelled before deposition. If this distance is sufficiently great, the effects of pollution are international or even intercontinental issues. The same characteristics determine how far particles follow the flow of inhaled air into the respiratory system, and whether the particles are retained in the nose, bronchi or lungs, or are simply exhaled harmlessly. Light absorption and scattering by particles influence the visibility of distant objects in conditions of haze, the colour of the sky (when cloud is absent) and the appearance of the landscape. The bibliography includes a few references that provide more detail of the general properties and effects of aerosols.

2.2 FORMATION OF AEROSOL PARTICLES

2.2.1 Size Scale

The mechanism of formation is crucial in influencing the size of aerosol particles. Several distinct mechanisms contribute particles to the atmosphere, and as a result the atmospheric aerosol spans a very wide range of sizes. The mechanisms operate differently for various materials and as a result the composition varies markedly over the size range.

The units used to describe aerosol particles, and the range of sizes involved, are illustrated in Figure 2.1. The range of sizes encountered is limited at the lower end by the size of a cluster of half a dozen or so molecules: this is the smallest entity of the condensed phase that can exist. The upper limit of size is approximately the size of a sand grain. Such particles fall quickly to the ground and normally travel only short distances while airborne. They cannot be properly described as suspended in the air except in extreme, high wind conditions.

2.2.2 Condensation and Nucleation

The finest particles result from the condensation of small numbers of involatile molecules. They may be formed in combustion processes and in evaporation from hot surfaces. Smokes and fumes from metallurgical processes, coal and oil burning, motor engines and even electric fires and cookers, contain numerous particles in this size range. Such particles also may result from gas-phase reactions (such as oxidation of SO_2 to form H_2SO_4) in the free atmosphere that form involatile molecules.

When molecules of an involatile substance are present in concentrations that far exceed the saturation vapour pressure, they have a strong tendency to condense. If a molecule encounters other molecules of the same substance it may combine to form a condensation nucleus - a very small particle. The molecule may meet a nucleus that already exists, or a particle of another substance, and condense causing growth in size. In practice nucleation is self-limiting, since once a sufficient number of nuclei have formed, further condensation is likely to occur on existing nuclei rather than form new ones.

These very fine particles (of order 1 to 10 nm diameter) are very light (see Figure 2.1). Where measurable concentrations of vapour condense in smoke or fume, they are generated in vast numbers - 10^5 to 10^6 per cubic centimetre of air is common in urban and industrial regions. They collide as a result of their rapid Brownian motion, adhere and agglomerate to form larger droplets, or the long dendritic chains of particles commonly seen in smoke. Further involatile matter, such as the sulphuric acid formed in sulphur dioxide oxidation, may condense on these particles. These processes gradually result in particles in the ‘accumulation mode’, roughly 0.05 to 2 µm diameter.

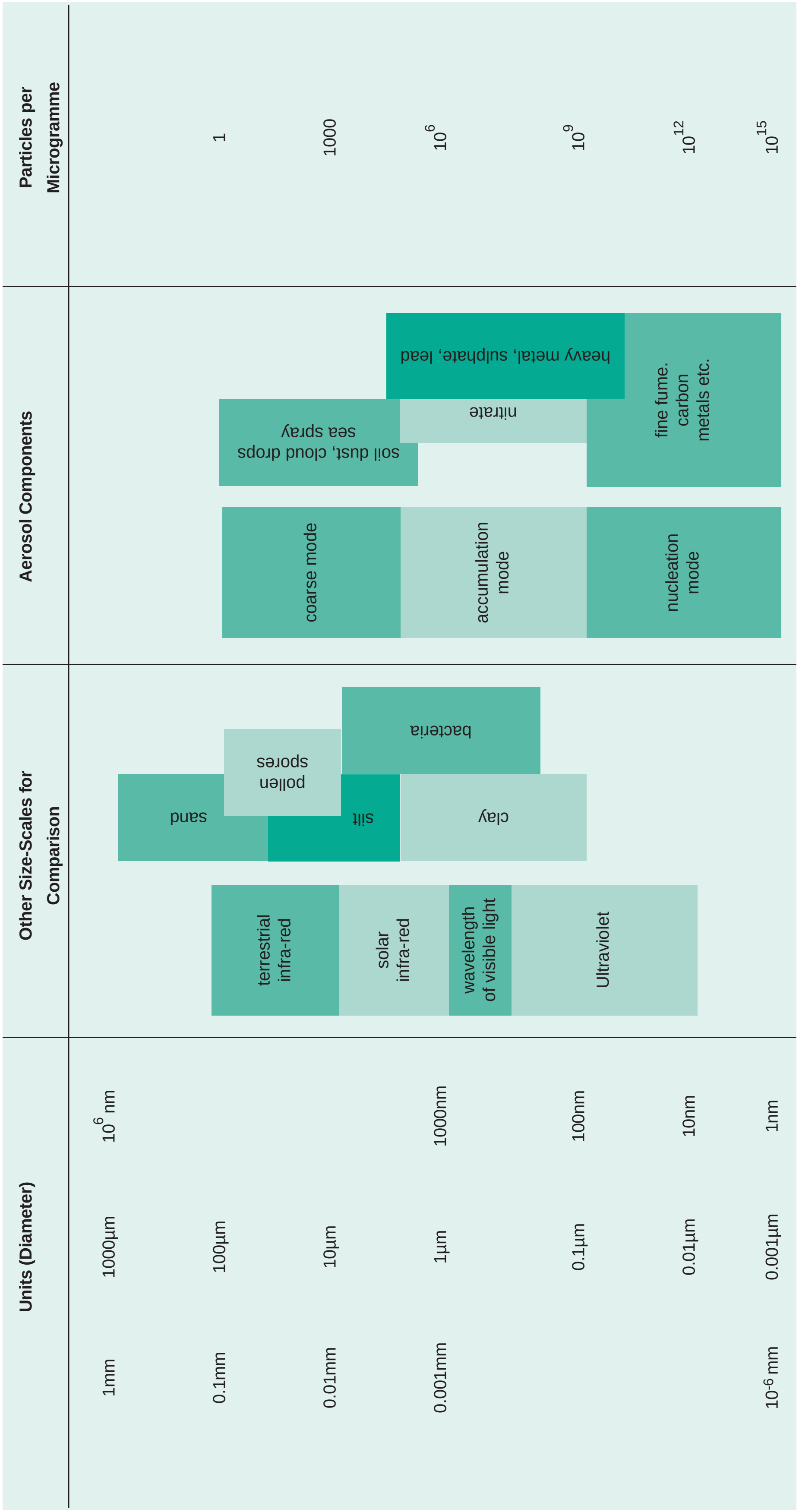


Figure 2.1 Aerosol Size-Scales.

2.2.3 Comminution

A number of processes reduce massive material to fine particles: the energy requirement depends on the surface area of the particles produced and the large amount of energy that would be required to generate great numbers of very small particles is usually prohibitive. In practice particles smaller than about 5 µm diameter are rarely generated this way, although evaporation of spray drops may result in particles a few times smaller.

In the natural world, various mechanisms result in the fragmentation of rocks, the dispersal of soil in the air or the formation of sea spray. Often wind energy is the agent involved in the final step of rendering particles airborne, and often in the fracturing of bulk material.

Man intensifies this process locally by various activities including quarrying, crushing and grinding of ores and other substances, raising dust in agriculture and road transport, spraying etc. In general, the result of artificial or natural dispersal of dust and spray in the atmosphere is a peak in the size distribution in the aerosol in the region of 10 µm diameter.

2.2.4 Fly Ash

This is a significant source of aerosol in some areas and is worth a special mention. Strictly, fly ash is a special case of a comminution aerosol. The fuel is reduced to small dimensions by crushing (coal) or spraying (oil) and suspended in the flame. Carbon and organic matter is lost by oxidation to leave involatile components as particles, which often show evidence of melting. This aerosol component is often accompanied by a fine condensation aerosol.

2.2.5 Cloud and Cloud Chemistry

Although rain and other forms of precipitation result in removal of a large fraction of the aerosol particles from the atmosphere, many clouds do not produce rain, and precipitation is frequently seen to evaporate before reaching the ground. Chemical processes within cloud droplets produce additional aerosol material. Cloud droplets condense onto pre-existing aerosol particles, and the result of droplet growth, cloud chemistry and evaporation is therefore expected to increase the size of the particle and perhaps to change its composition. Similarly, in cloud there are increased opportunities for aggregation of aerosol particles, with further growth in size. There is also some evidence that nucleation (probably of sulphuric acid solution droplets) is favoured at the high relative humidities within or close to clouds, where new, small particles are formed. The effects of clouds on the size distribution have not been quantified, but it is likely that particles chiefly in the accumulation mode increase in size as a result of cloud processes.

2.2.6 Size Distribution

The atmospheric aerosol shows evidence of the several categories of sources in its size distribution. Typically, three major components are recognisable:

The first (nucleation mode) is attributable to the nucleation process described above. This may contain very large numbers of particles of ~10 nm diameter, but because of the small size of each particle the mass in this component is often a small fraction of the total aerosol mass concentration.

The second component is often called the accumulation mode. Particles roughly in the size range 0.05 to 2 µm diameter are long-lived in the atmosphere since the removal mechanisms are least efficient in this region (see section 2.3 below). Coagulation and condensation leads to growth of particles in the nucleation mode into this region, and often a significant fraction of the aerosol mass accumulates in this size region. Particles in this size range are important vectors for long range transport (because they are long-lived) and are efficient light-scatterers, so they are often dominant in optical effects such as visibility.

Finally, the coarsest particle peak in the atmosphere comprises particles of ~10 µm extending to about 100 µm in diameter. These are shorter-lived, very variable according to local conditions, and are likely to travel distances typically of metres to hundreds of kilometres according to size and wind speed. They may contribute substantially to aerosol mass, although the number of such particles is often small.

These components can overlap to comprise the broad size distribution observed in the atmosphere (eg Figure 2.2). The greatest number of particles is almost invariably in the region smaller than 0.1 µm diameter. The mass of particles is predominantly in the accumulation and coarse particle regions, which may make comparable contributions to the total. Even the most remote, unpolluted parts of the atmosphere contain particles at total concentrations of order 300 per cm^3 of air, while urban air may have number concentrations about 1000 times larger.

2.3 PROPERTIES AND BEHAVIOUR OF AIRBORNE PARTICLES

2.3.1 Fundamental Principles

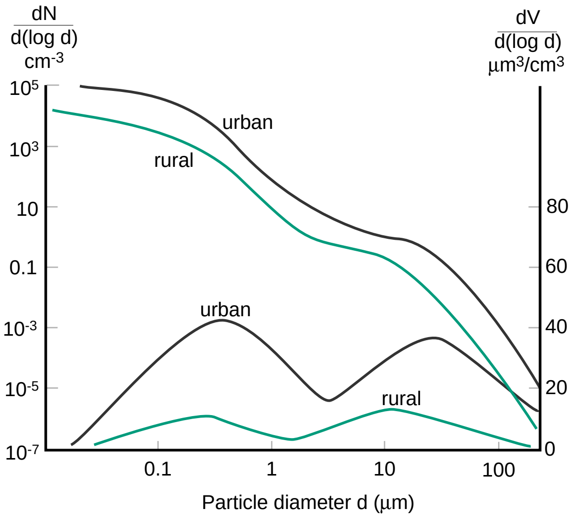
The physical properties of small particles, suspended in air, provide the scientific background for understanding the behaviour of the atmospheric aerosol. In this section some of the relevant physical properties are introduced.

(i) **Brownian Motion**: Small particles suspended in still air are seen to move about erratically. This motion results from the variations in the number and directions of impacts of air molecules on the surface of the particle. The smallest particles are most responsive to the tiny impulses from individual molecular impacts, and the effect decreases with particle size (see Figure 2.3).

The random motion that results causes particles to disperse slowly in still air, and to collide with each other and with surfaces: they adhere when they touch, and these contacts result in coagulation to form larger particles, and deposition onto surfaces.

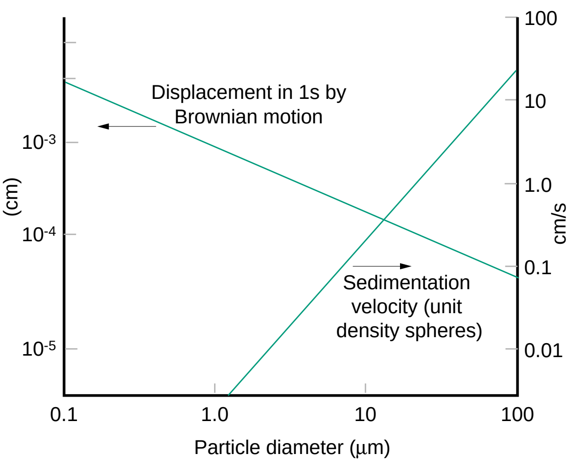
(ii) **Sedimentation**: Solid and liquid particles are about 1000 times denser than air at ground level. They cannot be buoyed up by the air and must fall through it, whatever their size. However, the gravitational settling of the particles is resisted by the viscosity of air, and each particle falls at a constant rate determined by its shape, size and density. The turbulent fluctuations in wind speed near the ground include upward motions but these are rarely much faster than 50 cm/s. Particles that fall through the air

Figure 2.2 Typical Size Distributions of Atmospheric Aerosol in Urban and Rural Areas.



Source: based on Jaenicke, 1993.
Note: The upper curves indicate number distributions, on a logarithmic scale (left hand scale). The lower curves indicate volume distributions (right hand, linear scale), roughly equivalent to mass distribution in units of µg/m^3.

Figure 2.3 Sedimentation Velocity and Brownian Motion, as a Function of Particle Diameter.



as fast as this cannot be lifted far away from the ground surface, and if raised by some disturbance must soon fall out.

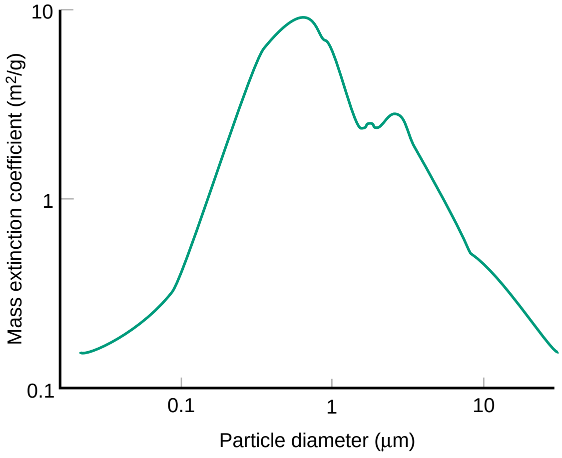
(iii) **Impaction**: Close to the ground the wind must flow around obstacles, such as the leaves and stems of trees and grass, irregularities in the soil surface, as well as buildings and other man-made objects. The inertia of the larger particles present in the air prevents them from following the flow around some obstructions to flow. The particles impact against obstructions and may adhere or (usually less often) bounce. The efficiency of this process increases with the air velocity, and particle size, and decreases with the size of the obstacle.

This process is significant in contributions to the deposition of particles onto surfaces, but also is used in sampling particles for measurement. The commonest size-selective samplers are cascade impactors, in which the largest particles are collected first by impaction from a jet of air, usually against a flat plate. In subsequent stages of the instrument, progressively faster air jets separate progressively smaller particles onto impaction plates. The aerosol is size-segregated according to its inertial characteristics. Strictly, the separation depends also on density and particle shape, and the result is specified in terms of the ‘aerodynamic diameter’ which is the size of a spherical particle of the same density as water with the same inertia.

(iv) **Interception**: Small particles following the airflow around an obstacle may make grazing contact with the surface just because the flow brings them within touching distance. This is an inefficient process, partly because viscosity retards the flow so close to the surface. However it is enhanced by the presence of fine surface structure (leaf hairs, surface roughness of soil, building materials etc) and is important for particles for which Brownian motion and impaction are inefficient.

(v) **Optical Properties**: Impairment of the visual quality of the atmosphere due to haze is often the most immediately apparent effect of air pollution. Particles may both absorb and scatter light, and both affect the visibility of distant objects and the appearance of the sky and landscape. Only particles containing elemental carbon (soot) absorb light significantly, and scattering is by far the dominant process. Even the molecules of clean air scatter light to some degree, explaining the blue colour of the sky in clear, unpolluted conditions. Molecular scattering (and scattering by the smallest particles) is much more effective for blue light than red, being proportional to the fourth power of the ratio (radius/wavelength). For larger particles, the dependence on radius is more complex. When the radius becomes similar to the wavelength, interference between light, refracted through various parts of the particle and diffracted around its edges, causes peaks and troughs in the total scattering, and complex patterns in the distribution of scattered light. Particles a few times larger than the wavelength scatter light equivalent to twice their cross sectional area. When particle mass is taken into account, the most efficient scattering is achieved by particles close in size to the wavelength (Figure 2.4). Scattering by such particles is not much affected by wavelength - hence the whitish appearance of dense haze.

Figure 2.4 **Mass Extinction Coefficient, as a Function of Particle Diameter.**



Source: Based on Harshvardhan, 1993, Ch 3 of 'Aerosol-Cloud-Climate Interactions, (PV Hobbs, ed) Academic Press, London and New York.

Note: The mass extinction coefficient (the example shown is for slightly absorbing spherical particles of refractive index 1.53-0.01i) is a measure of the effectiveness of particles in obscuring distant objects, or reducing the brightness of the direct beam from a distant light. For a given mass concentration, particles of about 0.3µm diameter have the most effect on light obscuration, and particles smaller than 0.1µm or larger than 1.0 µm are many times less effective.

(vi) **Uptake of Water Vapour**: Many aerosol particles consist largely of soluble matter. Sulphuric acid or ammonium sulphate and ammonium nitrate comprise a large fraction of the accumulation mode in industrialised regions, and sea salt is an important constituent in coastal regions. These hygroscopic substances take up water vapour at moderate and high relative humidities (Fig. 2.5). This results in an important increase in particle diameter, and influences many processes (light scattering, deposition) that depend on particle size.

In fog and cloud, the air cools until slightly supersaturated with water vapour. Each aerosol particle has a critical supersaturation: up to this point, the particle size increases with relative humidity (supersaturation is relative humidity minus 100%) maintaining equilibrium between the hygroscopic properties of its constituents and the effect of curvature of its surface, which favours evaporation. However, once the critical supersaturation is exceeded the particle continues to take up water vapour, limited only by availability of vapour. The particle grows to form a cloud droplet several microns in diameter. In practice, only a fraction of the larger aerosol particles grow to form cloud or fog droplets. They exhaust the supply of vapour before smaller particles reach their critical supersaturations. The effective particles are called cloud condensation nuclei, and are generally from the accumulation size range. Polluted air with large numbers of nuclei results in fogs or clouds with large numbers of small droplets; speculatively, these have greater persistence and opacity, and reduced likelihood of rain.

2.3.2 Deposition

A combination of processes removes particles from the air to the surface of the earth. Rain collects particles from the atmosphere, as can be demonstrated by analysis of samples of rainwater. Independently of rain, snow and other forms of precipitation, particles are brought to earth by gravity and by several other processes, collectively called dry deposition. Wet deposition, dependent on precipitation, is episodic, since in the UK precipitation occurs less than 10 per cent of the time, but removes particles from a great depth of the atmosphere. Dry deposition operates continuously but only at the surface. Together these categories of deposition must account for removal of all particles in the atmosphere.

Figure 2.5a Illustration of the Growth of Hygroscopic Particles with Increasing Relative Humidity.

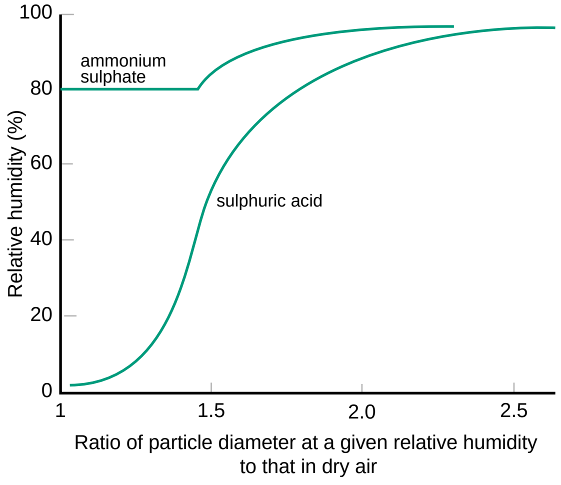
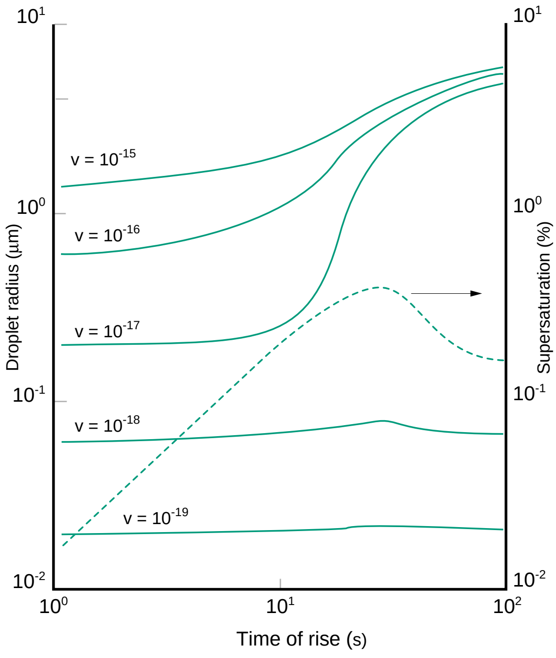


Figure 2.5b. The Growth of Cloud Droplets when an Aerosol of Sodium Chloride Particles of Different Sizes is Carried into a Cloud in a Steady Updraft. In this Example only Particles of 10^{-17} moles of NaCl or more Grow to Form Cloud Droplets.



Source: Adapted from BJ Mason, 1971, The Physics of Clouds, Clarendon Press, Oxford.

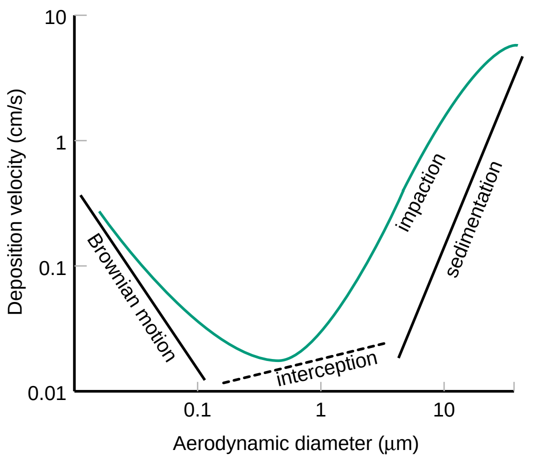
2.3.3 Dry Deposition

Near the surface of the earth, the air is mixed rapidly by turbulent motions, generated by the friction of the wind at the surface. The buoyancy of warm air, heated by contact with the surface in daytime adds to the turbulence, while, on clear nights cooling of the surface leads to an adjacent cold layer of air that inhibits turbulence.

The mixing distributes particles through the boundary layer, which usually extends to a height of about 1 km, and is the air layer that is directly affected by friction and heat exchange at the earth's surface. Away from the effects of sources the concentration in this layer would be roughly uniform with height, and in particular, turbulence maintains the concentration near the surface. However, immediately adjacent to a surface, air is retarded by viscosity and must flow parallel to the surface. Particles are carried though this layer, a fraction of a mm thick, inter alia by gravity, Brownian motion and impaction, or contact the surface by interception.

Once particles touch the surface, they are retained by surface forces (although large particles may bounce, they are likely to be trapped following multiple bounces). The combination of mechanisms and the resulting rate of deposition is illustrated in Figure 2.6

Figure 2.6 **Dry Deposition Velocity to Grassland as a Function of Particle Size.**



Note: The aerodynamic diameter indicates the inertial and sedimentation behaviour of particles, taking density and shape into account. The diagram shows how different mechanisms combine to remove small and large particles more effectively than those of intermediate size.

The deposition rate is generally expressed as the deposition velocity

$$V_d\ (\text{m/s}) = \frac{\text{Flux Density to the Surface (g/m}^2\text{/s)}}{\text{Concentration at Reference Height (g/m}^3\text{)}}$$

and the surface includes any vegetation, buildings or other features standing on a m^2 of land.

The deposition velocity depends on surface geometry, wind speed and atmospheric stability (the last is controlled by the heating of the surface by the sun, or its cooling at night) but the shape of the curve is generally much the same. The conspicuous minimum at about 0.05 to 2.0 µm diameter coincides with the accumulation mode size range.

2.3.4 Wet Deposition

Falling raindrops collect particles from the air that they traverse by much the same mechanisms. In particular Brownian motion, interception and impaction cause rain to scavenge particulate contamination from the air. As in dry deposition, the capture rate is minimum for particles roughly of 0.05 to 2 µm.

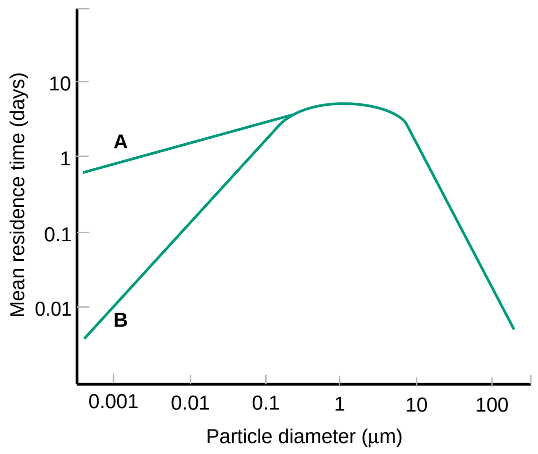
However, wet deposition is more difficult to investigate than dry deposition and our knowledge of wet deposition mechanisms is less complete. Processes within clouds differ from those below cloud in important respects. Rain clouds form in air that has risen from the surface, carrying moisture and aerosol from various sources. The droplets that constitute cloud form by condensation of water vapour on particles of roughly accumulation mode size, resulting in an order of magnitude increase in particle diameter. Generally in the UK, rain formation involves formation of ice crystals, larger than the more numerous water droplets, in the higher parts of the cloud. The falling ice crystals (or snow flakes) collect cloud droplets by impaction and interception before melting to form rain drops. Thus the particles involved as condensation nuclei have a high probability of being scavenged. Together with below-cloud processes, in-cloud scavenging ensures that all parts of the aerosol size distribution are subject to substantial removal rates during rain. Analysis of rain confirms that particulate tracers of all sizes are removed. Averaging wet and dry days together, the results imply an effective removal rate in rain over the UK of about 7% per day for particles of about 1 µm diameter and 15 to 30% per day for particles of 3 to 5 µm diameter and larger.

2.4 LIFETIME AND TRAVEL OF AEROSOLS

From the above discussion, it is possible to indicate the length of time that aerosol particles are likely to spend in the atmosphere (Figure 2.7). The smallest particles (1 nm diameter) last only for some 10 minutes, but their loss is due to agglomeration with other particles (and growth into the accumulation size range) and not loss of material from the atmosphere. In the accumulation size range, particles are likely to be removed from the lower atmosphere by rain in about 10 days (dry deposition alone would take 100 to 1000 days).

Larger particles (say 10 µm diameter) are likely to be airborne for 10 or 20 hours before dry deposition removes them. In the lower troposphere the mean wind speed is about 7 m/s, so the larger particles travel distances of 20 or 30 km while the smaller particles (0.1 to 1 µm) may travel several thousand km.

Figure 2.7 The Residence Time of Atmospheric Particles Entering the Boundary Layer.



Source: Adapted from Jaenicke, 1993.
Note: Curve A represents the deposition of aerosol particles to the ground, while curve B also includes the effect of coagulation, which reduces the number of small particles without removing their substance from the air.

Atmospheric conditions are very variable, and, while these values are useful to provide an indication of the average consequences of the emission of pollution to the atmosphere, they should be applied with caution to any particular event or trace substance.

A proportion of particles escape from the boundary layer to higher levels in the troposphere, often as a result of involvement in convective clouds or uplift of air in frontal systems. Those that are not removed in rain are likely to have longer residence times, due to the remoteness of the surface and the lower frequency of falling rain. The small fraction that reach the tropopause (about 8 to 15 km high) may remain airborne for times approaching a year.

The combined effect of persistence and transport of atmospheric aerosols was vividly illustrated by ^{137}Cs from the Chernobyl accident: the primary particles were measurable for over 2 months, showed a mean residence time of about 10 days, and reached all parts of the northern hemisphere.

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3 Measurement Methods

3.1 INTRODUCTION

There is a wide range of samplers available for monitoring particles. The choice though depends crucially upon the purpose of the monitoring. There are two basic reasons for particle monitoring that are dealt with in this Chapter:

- human health effects
- nuisance effects

In the case of human health it is the airborne concentration of particles that needs to be measured, while for nuisance effects it is principally deposited particles that have to be determined. The methods considered are designed to measure the quantity of material in the air or the amount deposited. Methods for chemical or physical analysis of collected particles are not covered.

The potential for particles to cause health effects is related to their size. Particles up to 100 µm enter the body during breathing, but it is only the very small particles, below about 5 µm aerodynamic diameter that can reach deep into the lung. It is widely accepted that it is these very small particles that have the main potential for causing health effects. It is therefore very important to define the size of the particles that are to be measured. It is no longer sufficient to measure what is termed “total suspended particulate” (TSP) or “suspended particulate matter” (SPM), as the size fractions being sampled are not specific but depend upon the equipment used to collect the sample. The current focus of health-related sampling of particulate matter is on PM_{10}, and this will therefore be the focus of the measurement methods described in this Chapter. There is also a growing interest in the finer fraction of particles, such as $PM_{2.5}$, so some consideration will be given to sampling of this fraction.

3.2 AIRBORNE PARTICLES

3.2.1 Scientific Framework

For health effects that are suspected to have arisen from particles entering the body through the nose and mouth during breathing, one must use a sampler whose performance mimics the efficiency with which particles enter the nose and mouth and penetrate to the region in the body where the harmful effect occurs. Workers in the occupational hygiene field have realised this for some years and defined the respirable fraction for those particles that penetrate to the alveolar region of the lung and cause diseases such as pneumoconiosis, silicosis, asbestosis, etc.

Since the early 1980s an ad-hoc working group of the International Standards Organisation has been formulating health-related sampling conventions for airborne dusts both in the ambient atmosphere and in the workplace. The final agreed conventions have passed through all stages of the approval procedure and should soon become available as International Standard IS 7708 (ISO, 1994). They are defined in Figure 3.1 and comprise four main fractions:

Inhalable Fraction (E_I) is defined as the mass fraction of total airborne particles which is inhaled through the nose and/or mouth. It was derived from wind tunnel measurements of the sampling efficiency of full-size tailor’s mannequins and replaces the very-loosely defined “total” aerosol fraction used previously. For ambient atmospheres it is given by:

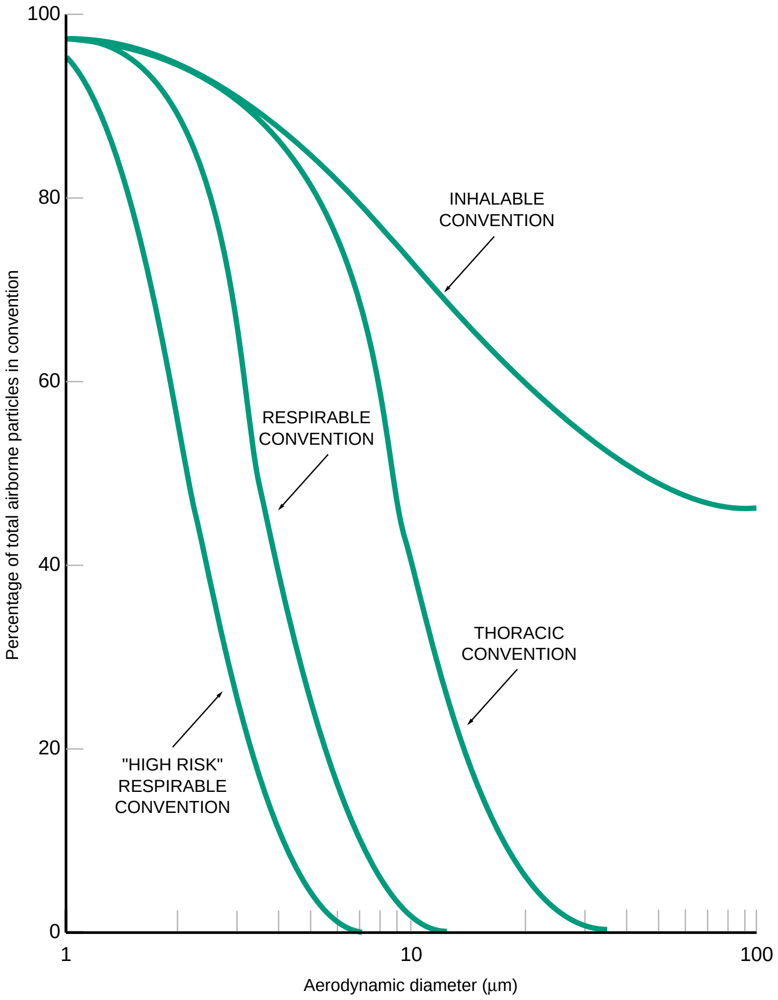
$$E_I = 0.5\,(1 + \exp\,[-0.06D]) + 10^{-5}\,U^{2.75}\,\exp\,(0.05D)$$

where D is the aerodynamic diameter of the particle (defined as the diameter of an equivalent spherical particle of density 10^3 kg/m^3,which has the same falling speed as the particle in question), and U is the windspeed (up to 10 m/s).

Thoracic Fraction is defined as the mass fraction of inhaled particles penetrating the respiratory system beyond the larynx. As a function of total airborne particles, it is given by a cumulative lognormal curve, with a median aerodynamic diameter of 10 µm and geometric standard deviation of 1.5.

Respirable Fraction is defined as the mass fraction of inhaled particles which penetrates to the unciliated airways of the lung (alveolar region). As a function of total airborne particles, it is given by a cumulative

Figure 3.1 ISO Health-Related Particle Sampling Conventions IS 7708 (1994).



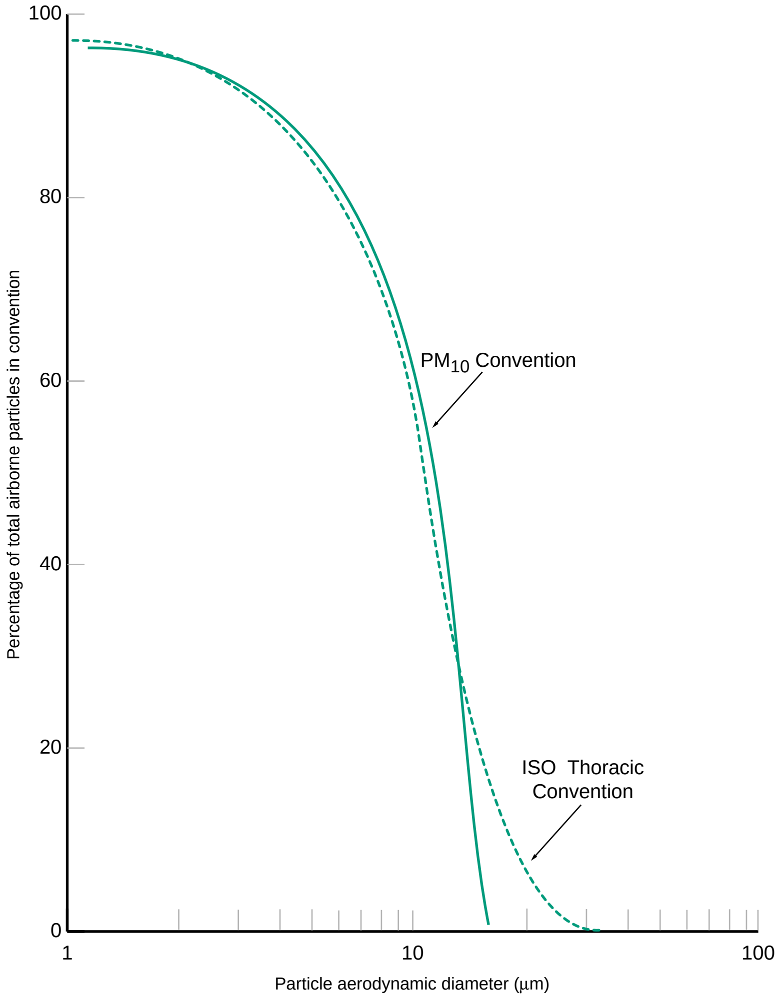
lognormal curve with a median aerodynamic diameter of 4 µm and a geometric standard deviation of 1.5.

`High Risk' Respirable Fraction is a definition of the respirable fraction for the sick and infirm , or children. As a function of total airborne particles, it is given by a cumulative lognormal curve with a median aerodynamic diameter of 2.5 µm and a geometric standard deviation of 1.5.

These conventions provide target specifications for the design of health-related sampling instruments, and give a scientific framework for the measurement of airborne dust for correlation with health effects. For example, the inhalable fraction applies to all particles that can enter the body, and is specifically of relevance to those coarser toxic particles that deposit and dissolve in the mouth and nose. The respirable fraction, on the other hand, relates to those diseases of the deep lung, such as the pneumoconioses, whilst the thoracic fraction may be relevant to incidences of bronchitis, asthma and upper airways diseases. Until recently, this philosophy has not been taken on board by the environmental community for health-related sampling.

In the European Union (and thus the UK), ambient airborne particle sampling has been guided by the Sulphur Dioxide and Suspended Particulate Directive (80/779/EEC). This Directive makes no reference to any particular health-related aerosol fraction. The measurement methods accepted are either for ‘black smoke’ or ‘suspended particulates’ by a gravimetric method. The EC Ambient Air Quality Assessment

Figure 3.2 PM_{10} and ISO Thoracic Particle Sampling Conventions.



and Management Directive, which has now reached a common position, sets out a number of pollutants to be covered by daughter Directives. These include “suspended particulate matter” and “fine particulate matter (including PM_{10})”. Technical work on these has now started within Europe.

There is a US EPA definition of the thoracic aerosol fraction known as PM_{10} (EPA, 1987), which has been systematically measured with validated instruments in the USA for the last 8-9 years. It differs slightly from the ISO definition in that its upper cut off is lower at 16 µm, as shown in Figure 3.2, although in practice this difference is not significant.

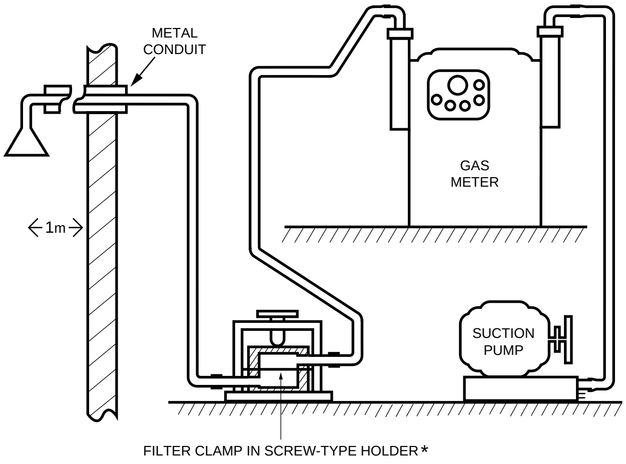
The USA is currently giving consideration to implementation of sampling for a finer aerosol fraction, with a median aerodynamic diameter of about 2.5 µm, which may eventually prove to be of greater health significance than PM_{10}. This would separate the finer particles of mostly anthropogenic origin from the coarser particles which include natural components. $PM_{2.5}$ sampling would equate to the high risk respirable fraction defined in IS 7708. Such samplers are already available and are starting to be used in the UK, although not in a routine way.

Ambient particle sampling currently focuses on the mass of the particles rather than their number. Recent suggestions that adverse effects of exposure to ambient particles may be caused by the ultrafine fraction (<0.1 µm) (Seaton et al, 1995), are likely to generate greater research interest in the measurement of particle numbers.

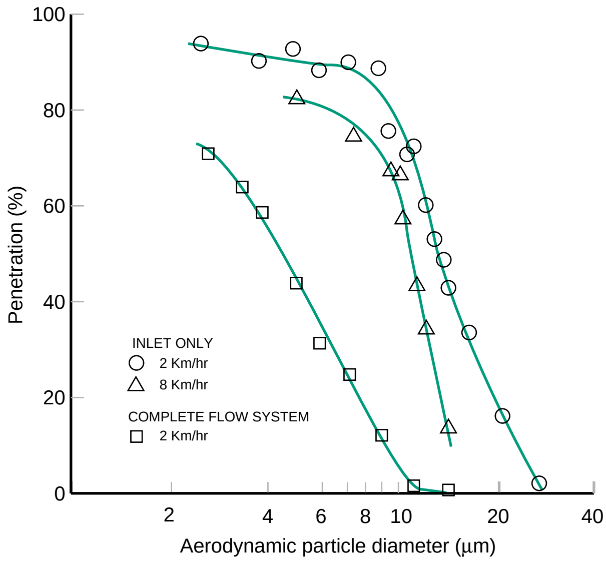
3.2.2 Early Techniques of Health-related Sampling of Particles in the UK

Sampling of ambient airborne particles was introduced into the UK on a routine basis in the first half of this century. In the 1960s the scale of sampling expanded rapidly, in response to the concerns about the health effects of the smogs. A countrywide network of simple samplers operated by local authorities was established to measure the levels of black smoke in the atmosphere. These samplers, shown in Figure 3.3, comprised a downwards-facing funnel into which air was drawn. The sampled particles were collected on a paper filter at some distance (typically 2 m) from the inlet. The quantity of dust was assessed by measurement of light reflectance from the surface of the filter. The black particles prevalent in the smoke from fossil fuels contributed most to the measurements at this time, which was converted to mass units using a calibration curve. This method was adopted by the British Standards Institute as the standard method for measuring airborne particulate matter (BSI, 1969a). It is still used today and is covered by the Sulphur

Figure 3.3 Components of British Black Smoke Sampler Together with its Sampling Efficiency.



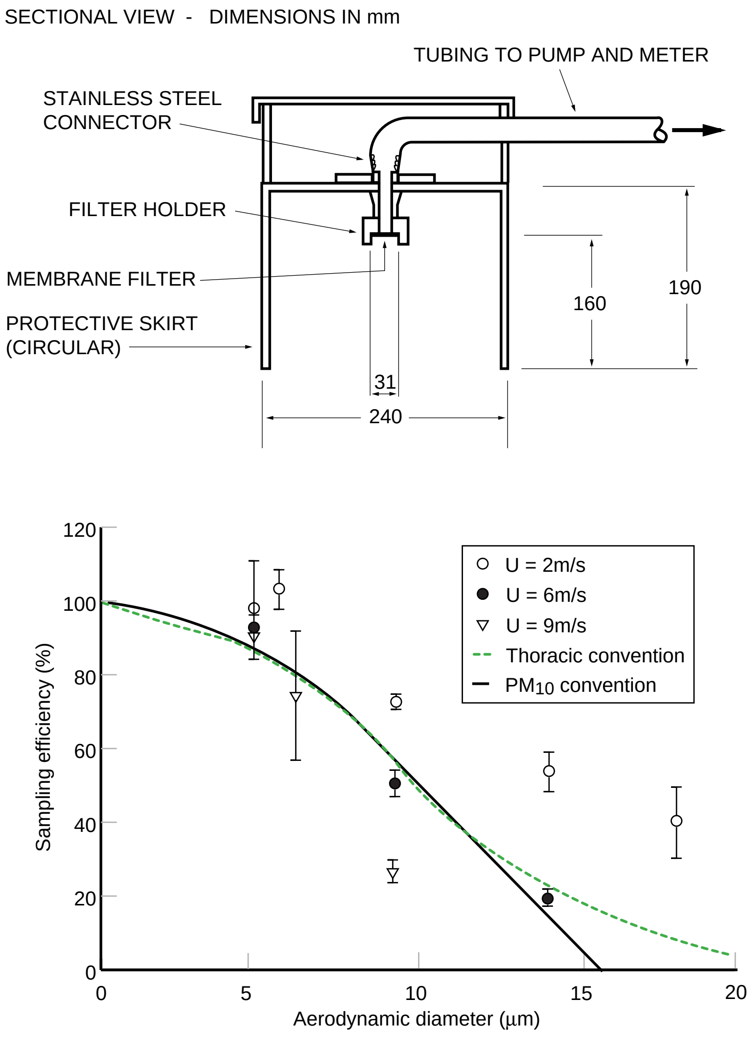
*STAINLESS STEEL STANDARD 47mm AEROSOL FILTER HOLDER ALSO USED



Dioxide and Suspended Particulates Directive (80/779/EEC). It should be noted, though, that the calibration curve in the EC directive differs from that in the British Standard (BS black smoke = 0.85 x EC black smoke). This is a useful reminder that the calibration of the black smoke method depends on the composition of the particles. For current particles, the black smoke method provides an indication of particle concentration but this is both site and season-specific. This can be seen in the comparisons between black smoke and PM_{10} measurements reported in Chapter 6. The sampling performance of the BS system (McFarland and Ortiz, 1984) is also shown in Figure 3.3, where it can be seen to collect particles below 4 µm with a high efficiency. It therefore approximates to the ‘respirable’ fraction defined in IS 7708.

In the early 1970s, the Government instigated two other national surveys of ambient dust to monitor sulphate aerosol and metals. Two very similar samplers were used in the surveys. The “S-type” for sulphate and the “M-type” for metals. The “M-type” sampler, is shown in Figure 3.4. It comprises a downwards-facing cylindrical hood covering a 37 mm open-face filter holder. The design was influenced primarily by the need to protect the filter from wind and rain. However, this inevitably meant that large particles were not sampled, as can be seen in the results of the wind-tunnel performance tests also shown in Figure 3.4 (Upton and Barrett, 1985). Its performance is strongly windspeed dependent, although at 6 m/s, which is close to the average wind speed in the UK, its sampling efficiency is close to

Figure 3.4 Details of M-type Sampling Head Together with its Sampling Efficiency.



that of a PM_{10} sampler. Although the M-type sampler is used in the UK for monitoring compliance with the EC lead directive (82/884/EEC) which sets an annual limit value, its performance characteristics clearly restrict its use as a health-related sampler over short time periods. However it may well be of value as an indicative PM_{10} sampler when the results are averaged over longer time periods, ranging from several months to a year. To support this view, results from monitoring in London over several years with the M-type sampler show annual mean concentrations that are very similar to those being measured with the PM_{10} sampler that forms part of the national network.

3.2.3 Samplers Designed to Monitor Health-related Particle Fractions

The majority of reliable instruments currently available are for the PM_{10} fraction. These generally make use of a validated sampling head to select the PM_{10} fraction of the ambient airborne particles, with the collected particles being analysed in two main ways:

1) Gravimetric, cumulative samplers in which the PM_{10} particles are deposited on a filter over a sampling period of normally 24 hours. The mass of particles collected on the filters is determined by weighing.

Table 3.1 Examples of Gravimetric, Cumulative PM_{10} Particle Samplers for the Ambient Atmosphere Currently Available in the UK.

Name	Flowrate l/min	Filter Diameter mm	Comments
PQ167 Portable PM_{10} Sampling Unit	16.7	47	Uses validated PM_{10} inlet (US EPA Protocol) connected to microprocessor flow-controlled pump. Battery powered - lasts for over 24 hrs using quartz or glass fibre filters
Partisol Model 2000 Air Sampler	16.7	47	Uses validated PM_{10} inlet connected to microprocessor controlled pump. Supplied as stand alone unit or with three additional satellites controlled by hub unit dependent upon wind speed and/or direction conditions
PM_{10} Dichotomous Sampler	16.7	37 (two)	Uses validated SA246b PM_{10} inlet followed by virtual impactor to give two fraction collected on filters; 10 µm - 2.5 µm and < 2.5 µm
PM_{10} Medium Flow Sampler	113	102	Medium flow rate sampler uses teflon or quartz filters, specially used for X-ray fluorescence and other compositional analyses
SA 1200 PM_{10} High Volume Ambient Air Sampler	1130	200 x 250	Standard sampler used in USA for PM_{10} aerosol in ambient atmosphere - high flowrate means short sampling times and large masses for gravimetric and chemical analysis

2) Direct-reading monitors in which the selected PM_{10} particles are either deposited on a filter, with continuous assessment of the change of a property of the filter due to their presence, or passed through an optical sensing region.

The $PM_{2.5}$ fraction can be measured using the same analysers, provided use is made of a $PM_{2.5}$ sampling head.

3.2.3.1 Gravimetric, Cumulative Samplers

These samplers basically comprise an omnidirectional rain-protected entry followed by a size-selective stage (normally an impactor) to separate the PM_{10} particles which are collected on the filter. There are a number of different samplers available, ranging in flowrate from 16.7 to 1130 l/min. A summary of the important features of some samplers available in the UK is given in Table 3.1 and a brief description of the design features and relative performance of the sampling heads is given below.

High flowrate samplers such as the Graseby Andersen PM_{10} Hi-Vol Sampler (see Figure 3.5) have been the mainstay of routine PM_{10} measurements in the USA. The high flowrate of 1130 l/min has the advantage of providing sufficient sample both for gravimetric and chemical analysis over the specified 24 hr sampling period. Hi-Vol samplers (without a complete PM_{10} inlet) were used in the Department of the Environment's national survey of dioxins, PCBs and PAHs in the ambient atmosphere (Coleman et al, 1995). The important features of the PM_{10} sampling head are an omnidirectional narrow slot entry, which samples particles independently of windspeed up to 10 m/s, and a multi-orifice single stage impactor, which allows the PM_{10} fraction to penetrate to a 25 x 20 cm filter. The efficiency of the sampler demonstrates full agreement with the US EPA PM_{10} Convention, as shown in Figure 3.5. The sampler is mains powered with either volume or mass flowrate automatically controlled. A high volume virtual impactor is available to insert between the impactor and the filter to provide the $PM_{2.5}$ fraction of the PM_{10} particles.

A number of low flowrate PM_{10} samplers are available in the UK. They all make use of the SA246b PM_{10} inlet developed and validated by Graseby Andersen. The entry (see Figure 3.6) consists of a flanged cylindrical pipe with a disc rain cap held some distance above. This forms the omnidirectional entry through which particles enter, followed by a single stage impactor which allows the PM_{10} fraction to

Figure 3.5 High volume PM_{10} Sampler Together with its Sampling Efficiency.

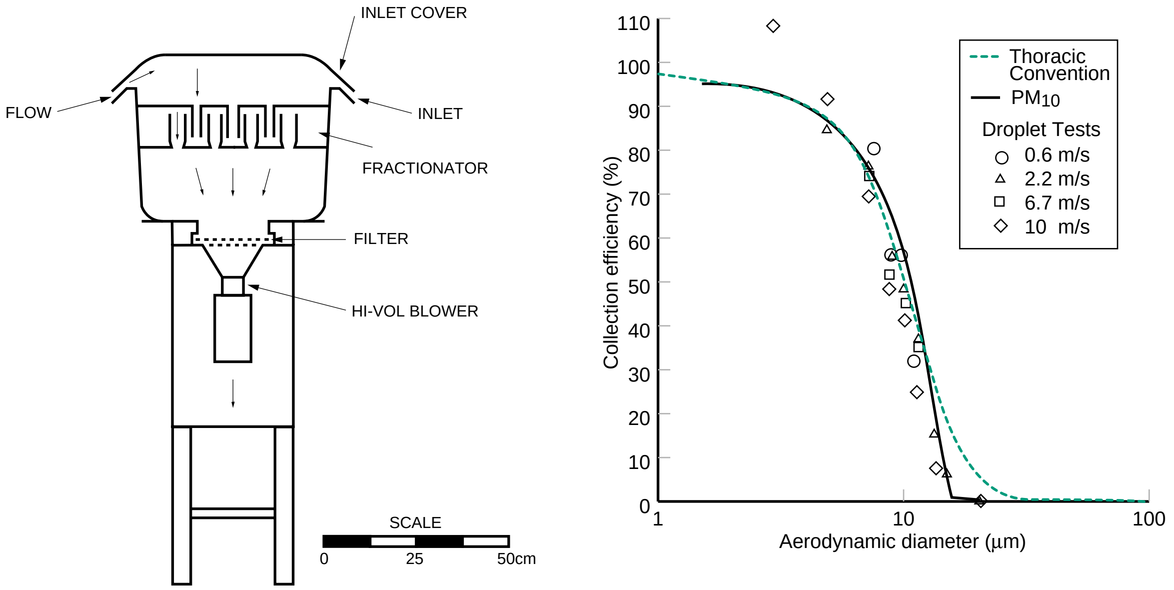
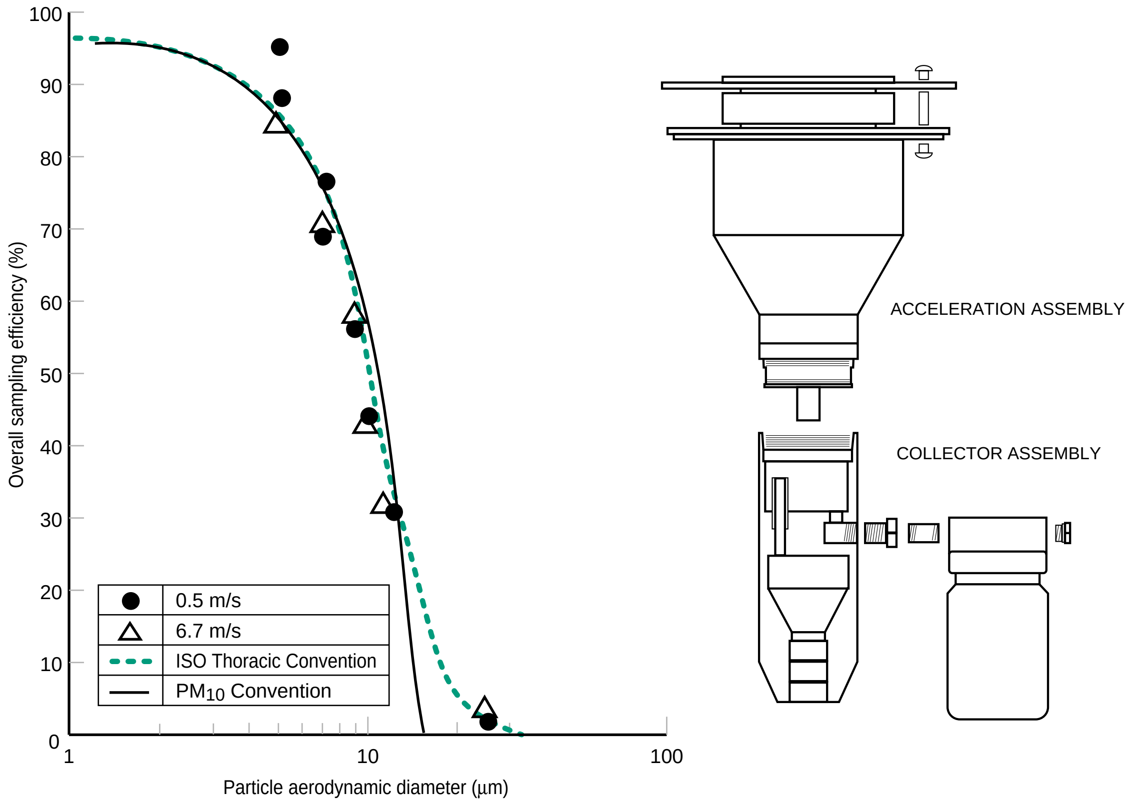


Figure 3.6 Low Volume PM_{10} Sampling Head Together with its Sampling Efficiency.



penetrate to a filter. The sampling efficiency of the entry, which demonstrates full agreement with the US EPA PM_{10} Convention, is also shown in Figure 3.6.

Three devices are included in Table 3.1, each having separate features that makes them to a certain extent complementary. The Casella PQ 167 Portable PM_{10} Sampling Unit uses a specially designed battery-powered pump which lasts for 24 hrs, and a 47 mm diameter quartz or glass fibre filter. This makes the sampler very useful at sites where mains power is not easily available.

The Rupprecht and Patashnick Partisol Model 2000 Air Sampler can either be supplied as a stand-alone unit or with three additional satellite PM_{10} sampling head and filter units. The satellites are connected to the main hub unit (at a maximum distance of about 3 m) through simple air flow lines which are switched via solenoid valves controlled by a user defined sampling programme. This enables four daily samples to be taken without attention. In addition, separate samples can be taken for different wind speeds, wind directions and at specified times, thereby providing useful evidence for source apportionment studies and for correlation with meteorological conditions. For all units the PM_{10} head can be replaced with a small cyclone inlet which has a 50% penetration at 2.5 µm. The sampler runs off mains power only.

Finally, the Graseby Andersen PM_{10} Dichotomous Sampler separates particles into two distinct fractions: 2.5 to 10 µm and < 2.5 µm. This is achieved by following the PM_{10} inlet with a virtual impactor with a 50% penetration at 2.5 µm, and collecting both fractions on 37 mm diameter teflon membrane filters. This gives some size distribution information of particles within the PM_{10} fraction, and provides separate samples for chemical species studies.

3.2.3.2 Direct-reading Monitors

For these instruments, sampling and analysis is carried out within the instrument, and the concentration can be obtained almost immediately. Like the low flowrate cumulative samplers described above, these instruments generally use the validated SA 246b PM_{10} inlet to select the PM_{10} particles which either deposit on a special filter stage or penetrate into a particle sensing region. Instead of direct weighing the presence of the particles either on the filter or in the sensing region gives rise to a property change, which can be related by calibration to the mass of particles present. A number of different instruments are available and these may be classified into three main categories: optical, resonance oscillation, and beta particle attenuation. A summary of the main features of the direct-reading instruments for health-related purposes is given in Table 3.2, and the principles of operation are described below.

Optical

These instruments employ the interaction between airborne particles and visible light in a sensing region, and generally their response is dependent upon the size distribution, shape and refractive index of the particles. They therefore require calibration to give results in terms of mass or number concentrations. This calibration only holds provided that the nature of the particles does not change and hence measurements obtained in ambient air are open to considerable uncertainty. Two instruments are currently available.

The DataRAM Portable Real-Time Aerosol Monitor uses a near infrared source and forward angle scattering to detect the concentration of particles in the range 0.1 to 1000 µg/m^3. It uses a scaled-down version of the SA 246b PM_{10} inlet to select the PM_{10} fraction at a flowrate of 2 l/min, although this has not been experimentally validated. The impactor stage can be replaced to give a nominal 50% penetration at 2.5 µm. The instrument is powered by a 6 V lead acid battery which lasts for 20 hours, making it useful at sites where mains power is not easily available. It is calibrated with AC fine test dust (mass median aerodynamic diameter 2 to 3 µm, standard deviation 2.5), and may need on-site calibration to ensure valid results in terms of mass concentration.

The Grimm Stationary Environmental Dust Analyser 1.200 comprises two samplers in one unit. The "reference" unit uses a standard 16.7 l/min PM_{10} inlet connected to a 25 mm diameter glass fibre filter. This is essentially a standard gravimetric sampler as previously described, with the concentration determined by weighing the filter. However an airflow splitter is used to extract air at 1.26 l/min downstream of the PM_{10} head, this sub-sample being fed into a light scattering optical particle counter. The optical counter uses peak height analysis to separate the particles into 8 channels in the range 0.3 to 15 µm. The mass concentration within these fractions is determined using calibration factors which can be determined from an in-built back-up filter (although a long sample period is required to collect sufficient sample on the back up filter with the low flow rate used). The optical particle counter is also available as a stand-alone unit as a nominal PM_{10} sampler. In this form it is particularly attractive because of its small size. It is a potentially versatile tool that provides both number and (nominal) mass size distributions. However, its performance as a mass sampler depends crucially on the calibration, which is based on integration over a long period and over all size fractions. It is not clear, yet, how variable the calibration factor is with time (hour by hour) and from one size fraction to another. Until these issues are addressed, the results from the optical unit must be treated with caution.

Oscillating Microbalance

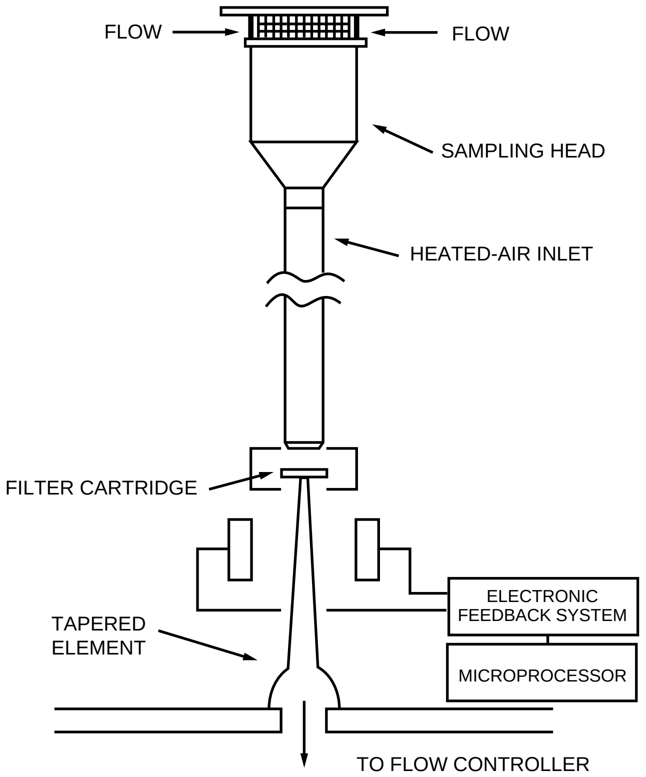
The frequency of mechanical oscillation of an element such as a tapered glass tube is directly proportional to the mass of the tube. Change in effective mass of the tube, such as that due to deposition of particles on the surface of a filter at the free end of the tube, is reflected in a change in its resonant frequency.

This is the principle of operation behind the Rupprecht and Patashnick Tapered Element Oscillating Microbalance (TEOM), as shown in Figure 3.7. A standard 16.7 l/min PM_{10} inlet selects the PM_{10} particles which pass through a flow splitter in which 3

Table 3.2 Examples of Direct-Reading Monitors for PM_{10} Particles in the Ambient Atmosphere.

Name	Measurement Technique	Flowrate l/min	Particle Fraction	Concentration Range µg/m³	Precision µg/m³		Comments
					1 hour	24 hours	
TEOM Series 1400a Ambient Particulate Monitor	Tapered element oscillating microbalance	16.7 thro inlet with 3 thro' filter/ detector	PM_{10} with possible 2.5 or 1.0 µm	0.06 - 1500	1.5	0.5	Only direct-reading monitor in which output directly related to mass. Employed as particle monitor at national Automatic Urban Network Sites.
W & A Beta Gauge Automated Particle Sampler	Attenuation of beta rays by particles collected on a filter	18.9	PM_{10}	$4 - 10^4$	4	0.1	One of a number of filter tape based beta gauges - measurement cycle 1 hour.
Airborne Particle Monitor APM1	Attenuation of beta rays by particles collected on a filter	15 - 30	PM_{10} (non validated)	$2 - 10^7$	56	2	Cassette system with 30 filters in sequential loader. Integrity of each sample maintained for compositional analysis.
GRIMM Model 1.104 Dust monitor	Light-scattering photometer	16.7 thro' inlet 1.26 thro' detector	PM_{10} with EPA validated head	$1 - 5 \times 10^4$ indicated	Not given	Not given	Optical particle counter with in-built filter for on-site calibration, as response may be dependent upon refractive index and size of particles.
DataRAM Portable Real-Time Aerosol Monitor	Light-scattering photometer	2	PM_{10} or $PM_{2.5}$ (non validated)	$0.1 - 10^3$ indicated	1.0	Not given	Optical device calibrated with AC fine test dust. May need on-site calibration to give reliable mass measurements as response dependent upon refractive index and size of particles. Entry dependent upon windspeed.

Figure 3.7 **Schematic Diagram of Rupprecht and Patashnick TEOM Ambient Aerosol Monitor.**



l/min passes through a 16 mm diameter filter connected to the top of the narrow end of a hollow tapered glass tube. As the particles collect on the filter, the tube's natural frequency of oscillation decreases. The change in this frequency is directly proportional to the added mass. The inlet including the sensing system is kept at a steady 50°C to drive off any sampled water droplets. The instrument is microprocessor controlled and the mass concentration values are updated every 13 seconds with average concentrations provided every 30 minute or every hour. This instrument is the particulate monitor chosen for the Department of the Environment's Automatic Urban Network sites and has been used by many organisations both in the UK and worldwide. Some concern has been expressed about the potential loss of volatile material at the stable temperature of 50°C (Weiner, 1995).

Beta Particle Attenuation

This involves the measurement of the reduction in intensity of beta particles passing through a dust-laden filter or collection substrate. The change in attenuation reflects the rate at which particles are collected on the filter and hence the concentration in the sampled air. The mass of particles collected is calculated from a knowledge of their mass absorption coefficient. The instrument is calibrated using the mass absorption coefficient for quartz. Measurements with ambient aerosols suggest the mass absorption coefficient may in practice vary by up to ±20%. The beta attenuation method is therefore inherently less accurate than gravimetric methods. Two main types of instrument have been developed: one using filter tape to collect the particles, and the other using a stack of conventional filters in a sequential loader.

There are many tape-based beta particle attenuation devices available, and details of just one typical example are given here.

The Wedding & Associates Beta Gauge Automated Particle Sampler uses their version of the low volume, validated PM_{10} inlet at 18.9 l/min to select the PM_{10} particles which are deposited on to either a glass fibre or PTFE filter tape. A beta particle attenuation system comprising a 3.7 MBq ^{14}C source and a fast response silicon semiconductor detector is used to detect the presence of dust on the filter with a one hour measurement cycle.

The Elecos Airborne Particle Monitor APM-1 is an interesting alternative to the tape based beta particle attenuation monitors. Instead of the filter tape, it deposits PM_{10} particles onto one of thirty 47 mm diameter filters held in a sequential loader system. This prevents violation of the integrity of the deposited particles enabling subsequent unambiguous gravimetric and chemical analyses to be made.

Beta particle monitors have been widely employed in a number of European countries. Further evaluation of Beta particle monitors by setting them up alongside a TEOM is however desirable.

3.2.3.3 Health-related Samplers for Coarse Particles

Particles as large as 100 µm can enter the human nose and mouth during breathing. Whilst the occurrence of these large particles may be rare, they can occur close to industrial processes and during periods of high windspeeds. Once inhaled they will deposit in the nasopharyngeal region and if toxic (such as lead, radioactive particles, etc) may enter the blood system there or in the gut.

The relevant ISO health-related fraction is the inhalable fraction, for which there is currently no commercially available instrument. The old “total suspended particulate” (TSP) was effectively defined by the “high-volume” sampler used to measure this parameter. The performance of this well-known device is both orientation and windspeed dependent, with its efficiency falling well below the inhalable aerosol convention, especially with large particles (Wedding et al, 1977).

Recent work has been carried out to develop a sampler to match the requirements of the ISO Inhalable aerosol fraction (Mark et al, 1990). It uses a single orifice that rotates through 360˚ (see Figure 3.8) to make it omnidirectional. A protective canopy protects it from rain and snow. The efficiency, as tested in a large wind tunnel, at different wind speeds is shown in Figure 3.8 (Mark et al, 1990, 1994).

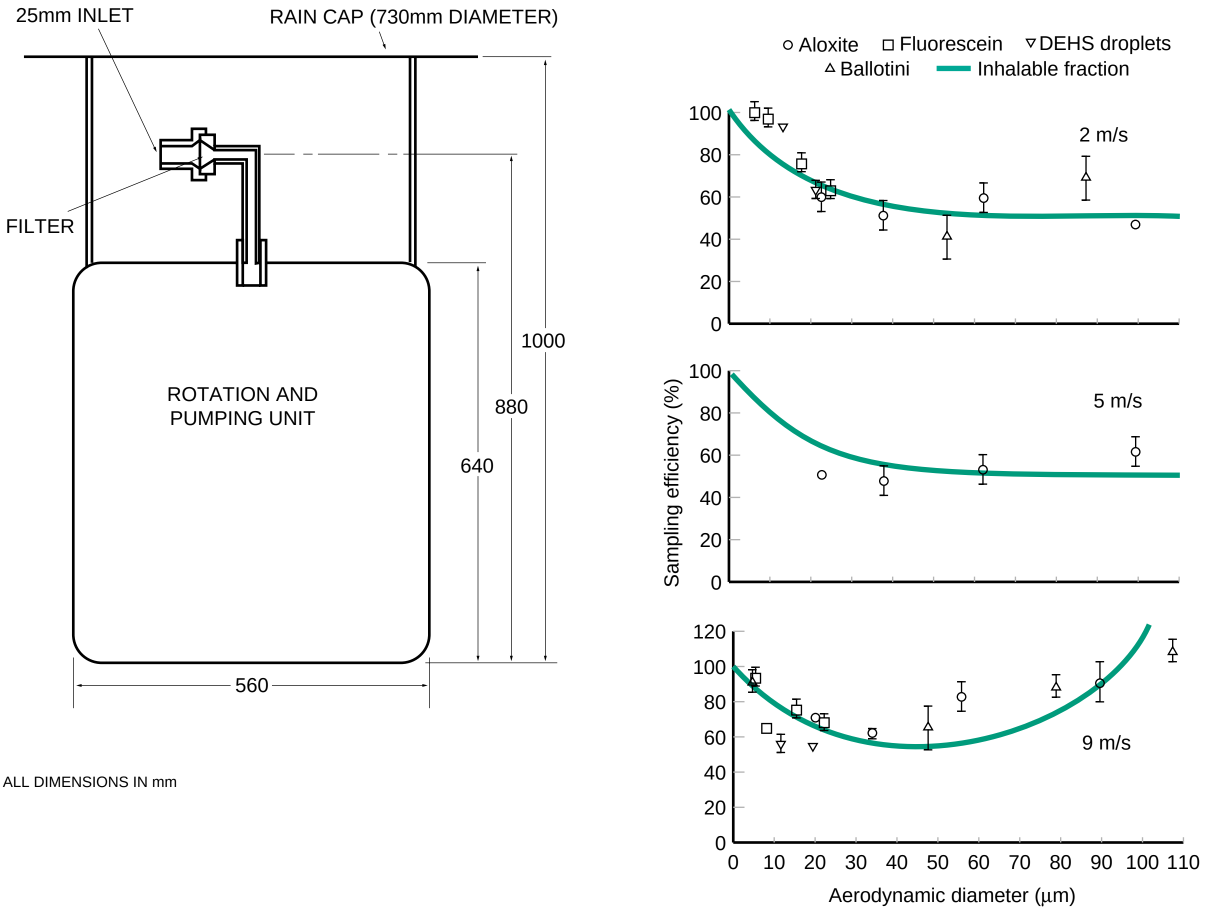
3.2.4 General Sampling Procedures to Monitor Health-related Particle Fractions

3.2.4.1 Selection of Samplers for PM_{10} Monitoring

The choice of samplers will be influenced by the timescale required for the measurement. The standard proposed by the Expert Panel on Air Quality Standards is 50 µg/m^3 as a rolling 24-hour average. This requires measurements to be made to a 1-hour timescale, with the 24-hour average being updated every hour. However, measurements of 24-hour concentrations over a fixed time frame will still provide a useful indication of air quality in relation to the proposed standard, but will underestimate the frequency and magnitude of exceedences. There is a range of samplers that meet the 1-hour or fixed 24-hour time frames, as indicated in Tables 3.1 and 3.2. The majority are relatively expensive, in the range £5,000-£20,000. Unfortunately there is no very cheap sampler available, as is the case with nitrogen dioxide, where the diffusion tube is now a widely used option to provide indicative results. The nearest equivalent for sampling of particulate matter is the ‘M Type’ sampler, which costs around £1,500. Its sampling characteristics make it a reasonable indicative sampler for long-term (eg annual average) PM_{10} concentrations, although other more expensive samplers with true PM_{10} inlets are preferable.

The TEOM is the sampler used in the UK Automatic Urban Network. It is relatively easy to operate once set up and provides concentrations resolved to 1-hour. It is however the most expensive sampler. Beta particle gauges are somewhat cheaper and the latest models are claimed to be capable of providing data resolved to 1-hour. As discussed above, their accuracy is probably not as good as the gravimetric samplers. The only other instruments capable of

Figure 3.8 CEC Ambient Inhalable Particle Sampler Together with its Sampling Efficiency.



producing time resolved data over 1-hour are the optical samplers, although there is still some uncertainty as to their accuracy as nominal gravimetric samplers.

The alternative approach to accurate PM_{10} measurement is the gravimetric sampler. These are somewhat cheaper than the automatic samplers to purchase, but set against this is the fact that they are labour intensive, in most cases requiring daily visits to change the filters, and access to a precision balance to carry out the weighing. The high-volume samplers favoured in the USA are more bulky and noisier to operate. These samplers are, however, all incapable of providing rolling 24-hour mean concentrations and there is an inevitable delay before results are available.

3.2.4.2 Sampling Strategy

Programme Types

There are two main types of programme:

1) Long-term studies at a number of fixed sites throughout the country to monitor pollution trends. At these sites a whole range of pollutants (including aerosols) are measured by continuous monitors with the results being sent by telemetry to a central data acquisition centre. Besides being used to monitor compliance with European Directives and the effectiveness of national policies, these programmes also provide invaluable data for public information and epidemiological studies.

2) Shorter-term studies designed to address a specific pollution problem. In these studies a large number of samplers are concentrated in a small area around a particular aerosol source, and measurements are normally taken before and after a specific operation has taken place. For instance, the construction of a new road, or a major industrial plant could result in significant dust exposures to the general public during construction but not before and after.

Sampler Location

The siting of the sampler has to take into account the purpose of the monitoring (QUARG 1993). For instance, is it to identify concentrations close to roads or is it to measure the more general urban background? Alternately, is it to measure the impact of a particular source, such as a construction site or mineral operation? Whatever the type of site, a number of general considerations need to be taken into account, including:

- obstructions to air flow caused by buildings, trees etc., which could introduce localised separations and swirls into the airflow and cause highly variable concentration gradients. These should be avoided wherever possible, especially if the larger particle fraction is being sampled.

- the height of the sampler entry above the ground. Ideally, for health-related studies the sample inlet should be at head height, although a compromise is often required for security reasons.

- for some samplers, including the TEOM, the sampler and sample head must be vertically aligned. This reduces the flexibility for site selection, especially at roadside locations.

Sampling Frequency and Duration

To ensure accurate estimates of likely human exposure, measurements should be carried out continuously. This is the approach used in the UK's Automatic Urban Network. The reason for this is that concentrations can vary considerably from one day to another. If shorter-term studies are to be carried out then they need to consider the daily and seasonal variability of particle concentrations. While a three month period of sampling should provide an estimate of the annual mean to within about 25%, it is likely to give only a poor estimate of peak concentrations, depending on whether or not any pollution episodes occurred during the sample period. In the USA, PM_{10} measurements have commonly been made using high-volume gravimetric samplers. These are labour intensive, as the filters have to be changed daily, and hence expensive to run. Because of this in the United States, in areas where the US limits are not exceeded, the sampling is carried out once every three days. This provides a statistical sampling of PM_{10} exposure, including exposure to peaks.

3.2.4.3 Operational Aspects

Most manufacturers supply comprehensive operational instructions with the instruments that they sell, and these should be read carefully before planning the details of the sampling programme. There are some general aspects, however, that merit mention here.

Choice of Filters

The choice of suitable filters for the gravimetric samplers mentioned above depends upon the sampling and analytical requirements. The most commonly used filters for sampling aerosols in the ambient atmosphere are glass fibre filters. These robust filters have low moisture retention, and high collection efficiencies at relatively low pressure drops. As the particles are collected in the depth of the fibre bed, glass fibre filters also have the ability to collect and retain large sample masses with a low pressure build up rate (and small change in flowrate). However, if compositional analysis or microscopic investigation of the collected particles is required, membrane filters are more suitable.

Membrane filters are made from a number of different materials with pore sizes ranging from 0.03 to 8 µm. For compositional analysis, cellulose nitrate or cellulose triacetate membrane filters are most widely used as they dissolve easily in organic solvents enabling the collected material to be recovered within a small volume of solvent for chemical analysis.

However, they are prone to weight changes due to moisture absorption, and more suitable membrane filters are made from PVC, which are widely used for quartz-containing aerosols, analysed by direct on-filter infra-red absorption techniques. Pure silver membrane filters are ideal for situations where impurities in the filter or high weight losses render normal membranes unsuitable. An example of this is in the sampling of coal tar pitch volatiles.

The other application where membrane filters offer distinct advantages is in the analysis of samples by microscopy. For optical microscopy, the filters are made transparent to light by the application of a liquid of the same refractive index as the filter. Polycarbonate pore filters (eg Nuclepore) are ideal for collecting particles for analysis by electron microscopy, but suffer from high electrical charge which can cause problems during weighing and very high pressure drop across the filter during sampling.

The main problem with all membrane filters is that, unlike glass fibre filters, particle collection takes place at the surface of the membrane filter. This severely limits the amount of sample that can be collected, because when more than a single layer of particles is deposited on the surface, the resistance to airflow increases rapidly. There is also a tendency for the deposit to be dislodged from the filter, especially during transport back to the laboratory.

Filter choice for continuous monitors is very limited. Beta particle monitors can be used with either glass fibre or PTFE filters, with the 30 separate filters contained in the cassette of the Elecos APM-1 device being especially suitable for analysis.

It is important to recognise that air filtration is not analogous to "sieving" and air filters can collect particles well below their nominal pore size with high efficiency. Nonetheless, filters with pore sizes of above about 2 µm may show appreciable efficiency limitations for small particles, especially at low surface loadings.

Filter Handling, Conditioning and Weighing

Important aspects that are often overlooked in the methodology of sampling are the handling and conditioning of the filters. When taking new filters from their boxes it is important to inspect the state of the surfaces. For instance, glass fibre filters often have loose fibres from the cutting process that could be easily lost at any stage of the sampling process. It is essential, therefore, that these are removed prior to the first weighing. In addition, some membrane filters have been seen with a very fine powder coating when new. Such filters should be rejected and a new batch used. When laden with dust, it is essential that the filters are supported and kept upright to prevent the loss of material that could arise from either sharp impact or touching the internal walls of the containers.

There are a number of schools of thought about the conditioning of filters prior to weighing. It is recommended that all weighing is carried out under temperature and humidity control, and that the filters are allowed to condition in that atmosphere for at least 24 hours both before and after sampling. The use of desiccators is not recommended, because when the filter is removed from the desiccator the weight will be unstable due to the absorption of moisture from the balance room atmosphere. A set of control filters to take account of changing conditions is highly recommended; one control for every five sample filters is a reasonable number to choose.

With annual mean mass concentrations of PM_{10} in the ambient atmosphere generally about 20 to 30 $\mu g/m^3$, care must be taken to ensure that the balance used has sufficient accuracy and precision. This normally requires a five-place or six-place balance. This should be placed on a solid, vibration-free bench in a room specially designated for this purpose, with temperature, and preferably humidity, control.

Flowrate Calibration

Besides the measurement of the mass of the collected sample, the most important parameter to determine accurately is the flowrate. Fortunately, most aerosol samplers are fitted with automatic flowrate control or compensating systems, in which the air velocity or pressure drop is continuously monitored and signals are sent via a feed-back loop to either open a valve or to increase the speed of the motor when they have changed by 5%. In the instruments made by Wedding and Associates, flow control is provided by means of a "choked" flow venturi system, which limits the flowrate to a maximum value provided that sufficient vacuum potential is maintained.

While flow control devices provide major improvements in maintaining the set flowrate throughout the sampling period, it is still necessary to set the flowrate before sampling can begin. Ideally this should be carried out by measuring the flow entering the sampling inlet using a calibrated wet gasmeter, but this is only possible for samplers with single unidirectional entries. For those omnidirectional samplers with horizontal slit entries, setting the flow rate is achieved by removing the entry and using a special fitting with an orifice plate over the installed filter. Once set to the correct value, the size selective entry is replaced and the flow control systems maintain the flowrate to within the specified limits (normally 5%).

3.2.5 Future Requirements

Currently, the PM_{10} fraction has been selected as the appropriate particle fraction to sample for health-related monitoring. However, it is thought that $PM_{2.5}$, or smaller fractions, may eventually prove to be of greater health significance than PM_{10}. Attention is likely therefore to focus on $PM_{2.5}$ samplers and possibly even on PM_1 samplers. Sample heads to separate out these fractions are already available and can be interchanged with those on existing PM_{10} samplers. The PM_{10} Dichotomous Sampler, which provides two samples - 10 to 2.5 µm and <2.5 µm, should be useful in this context.

For specific epidemiological studies, it may be necessary to use personal samplers to provide a reliable estimate of individual exposures to ambient particles. A number of samplers, developed initially for workplace sampling, could be used to monitor all three health-related fractions. A pilot study on behalf of the Department of the Environment is currently under way in Birmingham using prototype personal samplers for the thoracic fraction. The units are designed to be light and quiet, so as to minimise discomfort to the wearer.

An interesting new development is the Rupprecht and Patashnick Ambient Carbon Particulate Monitor. This device automatically determines hourly averages of organic and elemental carbon particulate matter concentrations. It therefore provides additional information on the composition of particulate matter on a fine timescale, which will help in the understanding of the sources of airborne particles.

Finally, suggestions have been made that the health effects of particles may be related more to particle numbers than to particle mass. This focuses attention on the ultrafine (<0.1µm) fraction, which can be sampled and counted using devices such as Condensation Nucleus Counters, which give number concentrations of particles down to below 0.01 µm.

3.3 NUISANCE DUST

Nuisance dust is generated by a wide range of activities, including traffic; construction/demolition; mineral workings; and industry. It can give rise to considerable public concern about the quality of their environment. Unfortunately, the term nuisance dust is not readily definable. It covers a number of effects, ranging from soiling of surfaces, such as window ledges and cars, to clouds of dust that can cause physical irritation. These effects have different attributes and different timescales, all of which means that no single measurement method is appropriate. The soiling of surfaces is generally a reflection of dust accumulated over a period of time, ranging from days to weeks, whereas the cloud of dust is a transient phenomenon, that may last a matter of only a few minutes.

The soiling aspect of nuisance dust is measured by collecting dust deposited on a surface. Two basic approaches have been adopted

- determination of the quantity of dust deposited, by weight

- determination of the soiling of a surface, by a change in its property

The short-lived dust clouds that can give rise to nuisance are not easily measured. Some form of measurement of total suspended particulates would seem appropriate. Most measurement methods deal with a minimum of 24-hour concentrations, although the TEOM and Beta particle counter produce 1-hour data (15-minute values can be obtained with the TEOM for high concentrations) (see section 3.2.3.2). Optical samplers may also have a useful role to play, because of their fine time resolution, especially in identifying dust clouds, where the issue of accuracy may be less important than knowledge that an event is taking place.

Deposit Gauges

There are two basic methods in common use. The first is the British Standard Deposit Gauge (BS 1747 Part 1), which has been in use for many years. This is essentially a large bowl, which is used to collect all material deposited over a one-month period. Many measurements were made in the UK using this method during the 1960s and 70s, and information was collated nationally until the early 1980s, since when data have not been reported. The second method evolved during the 1980s, based on work carried out by Warren Spring Laboratory. It uses an inverted frisbee as the collector. This is more aerodynamically sound in terms of its disturbance of the airflow, minimising the effect of eddies on the collection and loss of particles. It is also smaller and hence easier to use in the field. A third type of sampler, the Directional Dust Gauge (BS 1974 Part 5) has also been fairly widely used. This is a bundle of four vertical tubes with slots facing in four separate directions. The device is not a deposit gauge, but a means of measuring the horizontal flux of dust. It is used to indicate the direction from which dust is coming. Measurements with this gauge have not been related to nuisance effects.

The frisbee deposit gauge has been used fairly widely over a number of years, usually collecting weekly samples. The relationship of the frisbee to the British Standard gauge is, however, very uncertain, hence the relevance of the new data to previous findings cannot be judged. Wind tunnel testing showed the basic frisbee to be more efficient than the BS gauge (Hall and Upton, 1988), while tests in the field showed it collected 20-30% less than the BS gauge (Vallack, 1995). Variants of the frisbee have been used to help retain the deposited dust, including coating the surface with liquid paraffin and inserting a nylon mesh. Field tests have shown the coated frisbee to collect 15-80% more dust than the BS gauge, while the nylon mesh increased the collection by 2-11% in one study (Vallack and Chadwick, 1992) and decreased it by 2% in another (Vallack, 1995). The field tests have been limited and it is not clear how generally applicable the findings are. It is therefore not possible to use correction factors to produce BS gauge equivalent values. The frisbee with nylon mesh would appear, however, to be the closest to the BS gauge and hence the most relevant in terms of continuity with historic data.

Recently, the frisbee deposit gauge has undergone a further change (Vallack, 1995). It is now recommended that the gauge has a porous foam liner fitted. This is designed to trap the deposited particles and prevent them being blown out of the collector. Recent studies have been carried out comparing the new frisbee (which is now cast out of aluminium and has slightly different dimensions to a real frisbee) with both the previous design and the British Standard deposit gauge. The results showed that the frisbee with the foam insert collected 30% more than the BS gauge and 87% more than the basic frisbee. Yet further modifications have been proposed, including a flow deflector and a slightly deeper bowl (Hall et al, 1994). This new design has not been compared with previous gauges. These frequent changes in collector design make it essentially impossible to compare findings from one study to another.

A further major limitation of the deposit gauge as a measure of nuisance dust, is the lack of reliable criteria to assess the findings. Reference is frequently made to an annual deposition rate of 200 mg/m^2/day, although the basis of this figure has never been adequately traced. This value is said to represent the threshold for serious nuisance (Bate and Coppin, 1990). Several factors need to be borne in mind when considering use of this criterion:

- It was developed many years ago, at a time when the public's acceptance of dust was probably much more tolerant than now.
- There have been no recent studies to confirm its appropriateness to current public sensitivities about the environment.
- The literature contains a range of criteria from 133 to 350 mg/m^2/day (Bate and Coppin, 1990) and not a single figure.
- The details of the studies used to develop the criterion are not readily available, and hence it is not possible to establish how applicable the findings are today.
- The criterion is an annual average. It is therefore not valid to compare individual monthly or weekly values with this criterion. A shorter term criterion would be more useful for assessing the occasional dust incident.
- The nature of the dust plays an important role in determining its nuisance impact. For instance, it has been suggested that for coal dust a deposition rate of 80 mg/m^2/day is likely to give rise to complaints.
- The standard is based on the use of the BS gauge, and is therefore not directly applicable to results obtained with the frisbee.

It has been suggested that, given the unreliability of the 200 mg/m^2/day criterion, it would be appropriate to set a criterion for nuisance of two to three times the existing background deposition rate (Bate and Coppin, 1990). This has some merit, but there is no reliable published database of existing deposition rates, using either the British Standard gauge or the frisbee gauge, to act as the starting point.

Soiling Methods

An alternative approach to the deposit gauge is to measure the soiling of a surface. The advantage of this method is that it is a more direct measure of the nuisance effect caused by dust. It is also easier and cheaper to carry out the monitoring. One disadvantage, though, is that it is not possible to predict soiling rates, whereas it is possible to predict quantitative deposition rates.

There are two basic methods that are used. One involves exposing a white adhesive tape for a period of several days (Beaman and Kingsbury, 1981). The particles stick to the tape and the quantity collected is measured using a smoke stain reflectometer. The results are expressed as the percentage effective area coverage (ie percentage reduction in reflectance) per day. Typical soiling rates have been published, ranging from 0.01% EAC/day in rural areas to 1% EAC/day in industrial areas (Beaman and Kingsbury, 1981). However, recent measurements using this method indicate much higher soiling rates, averaging 0.7% EAC/day at urban fringe/rural sites (Coppin, 1995). The reason for these divergent results is unknown. Criteria have also been produced to assess the nuisance effect. It is claimed that possible complaints start at 0.5% EAC/day and serious complaints at 5% EAC/day (Beaman and Kingsbury, 1981), but the basis for these criteria has never been published. Comparisons have been made between soiling rates measured with the sticky pad and total suspended airborne dust (Beaman and Kingsbury, 1984). A soiling rate of 0.5% EAC/day equated to 34 µg/m^3, 1% EAC/day to 65 µg/m^3 and 5% EAC/day to 280 µg/m^3. It is not clear what time periods these measurements were made over, and hence how applicable the findings are to measurements over several days.

The sticky pad method has been used fairly widely, by a number of consultancies, and by British Coal. However, its wider acceptance is hindered by the lack of published data on the range of existing soiling rates or on the criteria for interpretation.

The second approach to the measurement of soiling rates is the glass slide method (Schwar, 1994). This is based on exposing glass microscope slides horizontally in the field for a week, then returning them to the laboratory to measure the reduction in reflectance at a 45˚ angle from the surface, using a gloss-meter. The measurement method is now commercially available. The results are expressed as a soiling rate in soiling units (su) per week. One soiling unit is a one percent reduction in reflectance. Typical soiling rates are around 10 su/week, rising to over 30 su/week close to very dusty activities. Criteria have been determined to establish public acceptability of different soiling rates. A rate of around 20-25 su/week, averaged over 4 weeks, appears to be the boundary between acceptable and unacceptable dust levels (Moorcroft and Laxen, 1990).

Concerns have been raised about material being washed off the glass slide, as the surface is not coated. In practice this is only a problem if there is extremely heavy rainfall. Generally, the dust adheres readily to the glass, even with moderate rainfall. In contrast to other methods, the glass slide is not designed to collect and retain all the dust deposited. The behaviour of this collector is designed to mimic the natural behaviour of dust on outside surfaces, such as the paintwork on cars, including the effects of removal and redistribution by rainfall. It is understood that some workers have modified the method to retain more of the dust, however, this invalidates any comparison of the findings with the acceptability criteria developed with the original method. The glass slide method has been compared with both dry frisbee measurements of deposited dust and airborne dust measurements using the M-type sampler (Moorcroft, 1995). No relationship was found between the frisbee and glass slide results. On the other hand, the glass slide results were positively related to those of the M-type sampler. This indicates that the glass slide method is measuring a different component of deposited dust to the frisbee deposit gauge.

It is clear from the discussion of the different methods of measuring deposited dust, that no consistent approach is yet available. One of the major problems with all the methods is the tendency for workers to continually develop modifications to the methods. This makes it difficult to build up a database of measured concentrations and of acceptability criteria. All methods also suffer from a dearth of published information on both existing levels in different settings and acceptability criteria. Without these features it is difficult to assess the findings of any of the available methods. There is a clear need for a standardised approach to measuring and assessing nuisance dust to be developed.

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NOTE TO READERS

This Chapter seeks only to indicate some of the equipment choices available to those wishing to measure airborne particulate matter. It makes no attempt to be exhaustive, and some commercial instruments have not been included. Omission of an instrument should not be inferred as conveying any opinion by the Review Group and equally, inclusion does not constitute an endorsement by QUARG.

4 Sources and Emissions of Primary Particulate Matter

4.1 INTRODUCTION

This Chapter describes the primary sources of particulate matter, and attempts to quantify their emissions. Secondary sources (formation in the atmosphere from other forms of pollution) are discussed in Chapter 5. The term “particulate matter” describes all particles present in the atmosphere, and includes both solid particles and liquid droplets (but not their water content). Unless stated otherwise, inventory data in this Chapter refer to the mass of particles in the PM_{10} size range, although some sources emit a substantial mass of particles of larger size. Particle numbers are not considered.

In comparison to other pollutants there are two features of particulate matter that increase the difficulty and uncertainty of estimating their emissions. The first is that the range of sources that emit particulate matter include, not just fuel use, but also fugitive sources whose scale and activity rates are poorly known. The other is the overlapping definitions of particulate matter. The size distribution of particulate emissions differs markedly from source to source. Other definitions of particulate matter such as “Black Smoke” do not have an unequivocal relationship with particle mass. In the literature, studies of particulate matter have used different definitions for what they mean by particulate matter and are thus difficult to compare. This Chapter will estimate emissions of particulate matter in terms of their PM_{10} mass.

Primary emissions of particulate matter can arise from many sources. The main sources are:-

Road Transport. This term refers to all road traffic. Emissions arise mainly from the exhaust, but tyre and brake wear also generate airborne particles. In general, diesel engined vehicles emit a greater mass of particulate matter per vehicle than those with petrol engines.

Stationary Combustion. Domestic coal burning is traditionally the major source of particulate matter emissions. This has now been restricted in major cities due to the Clean Air Acts but is still important in some smaller towns and villages, in Northern Ireland and in areas associated with the coal industry.

Industrial Processes. This includes bulk handling, construction and quarrying. These sources are difficult to quantify both due to the nature of the source and due to the lack of information on the extent of some of these activities.

Fugitive emissions relate to pollutant losses from points in a process not associated with a defined process stream (such as a stack). Such sources generate particulate matter through two main processes:

(i) Mechanical break-up through pulverisation or surface abrasion resulting in the production of dust. This can include tyre and brake wear, mineral processing, wear of wheels and blades and various construction activities.

(ii) Wind-blown dust. For example soil erosion or erosion of stockpiles by winds with speeds typically in excess of 5.4m/s (12 mph).

Temporary activities such as construction create particles from a wide range of cutting, grinding and crushing operations. Despite their temporary nature, construction sites can have a substantial impact on local air quality .

This Chapter looks at the main sources of primary particulate matter in the UK and their emission rates. It does not consider secondary production of aerosol. The problems and uncertainties in estimating emissions are indicated. Estimates of PM_{10} emissions for the UK and London are presented.

These estimates of primary PM_{10} sources differ from earlier estimates (eg QUARG, 1993) for a number of reasons. Firstly, revised PM_{10} emission factors for road transport have been used which are based on a greater amount of measured data. Secondly, estimates of non-fuel use sources are included (eg construction) and finally, all the other fuel use emission estimates have been reconsidered.

4.2 PRIMARY EMISSION SOURCES

4.2.1 Road Transport - Engine Emissions

Road transport is thought to be the major source of PM_{10} in urban areas. In general diesel engines emit particulate matter at a much higher rate than petrol engines. Whilst particulate emissions have been part of the European Union type approval emission test procedure for diesel engines, this has not been the case for petrol engines, and thus few measurements of exhaust emissions of particulate matter from petrol cars are available.

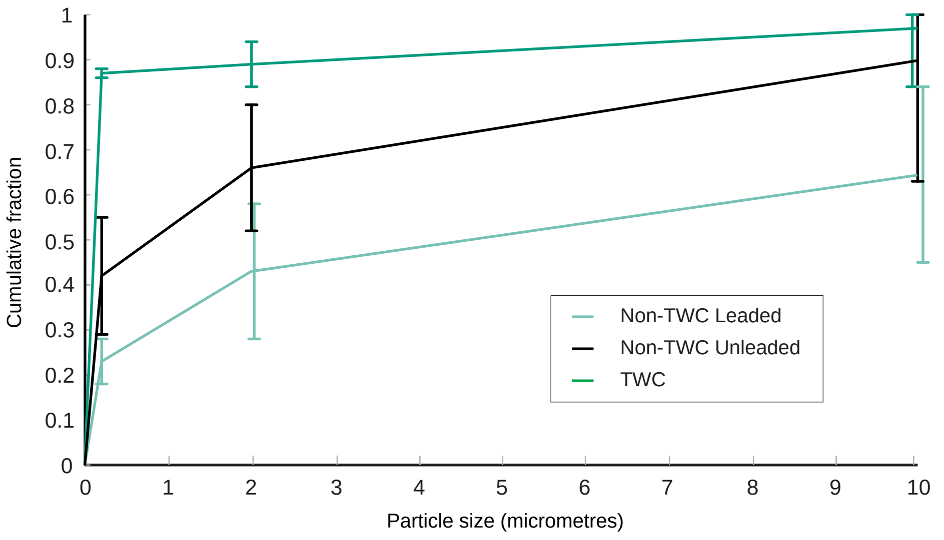
Diesel particles start their formation in the high temperature combustion process. Initially only soot particles of carbon are formed while the other compounds are in the vapour phase. The hydrocarbons and sulphate (which results from the fuel sulphur) condense as the temperature drops. The type approval test procedure requires that the exhaust is cooled to 52°C, at which temperature these particles consist of a carbon core with a coating of hydrocarbons and sulphate. Particles grow by coagulation, condensation and adsorption. These processes occur predominantly after the gas has left the exhaust pipe as the residence time in the pipe is too short for coagulation and the temperature too high for adsorption and condensation.

The particle size distribution tends to be bimodal with particles of 0.0075 to 0.050 µm diameter, in the nucleation mode, consisting of either carbon spheres or condensed liquid hydrocarbons, and an

Table 4.1 Size Fractions of Particulate Matter Emissions from Road Transport (from USEPA, 1985).

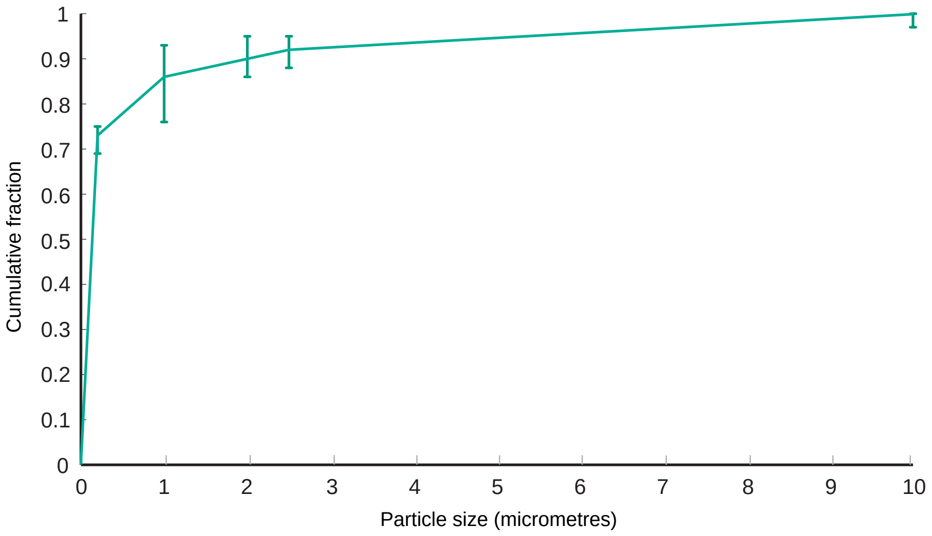
		Mass percentage in size fraction	
		< 2.5 µm	**< 10 µm**
Petrol cars	Leaded - no catalyst	67	80
	Unleaded - no catalyst	70	90
	Three-way catalyst	90	97
Diesel cars		92	100
Diesel HGV		92	100
Tyre Wear		39	55
Brake Lining		39	98

Figure 4.1 Size Distributions of Particulate Matter Emissions from Petrol Engined Cars (USEPA, 1985).



Note: Error ranges are 95% confidence intervals. The size axis has been displaced slightly for each curve for clarity.

Figure 4.2 Size Distributions of Particulate Emissions from Diesel Engined Cars (USEPA, 1985).



Note: Error ranges are 95% confidence intervals.

accumulation mode of about 0.05 to 1 µm diameter. (See Glossary for definition of terms).

The official European test procedure collects material on a filter through a heated line and so may not measure exactly the mass of particulate matter actually emitted into the atmosphere. Research shows that the sizes of diesel particles are virtually all less than 10 µm (Table 4.1, Figures 4.1 and 4.2) with particulate matter from the use of leaded petrol slightly larger (USEPA, 1990). The factors in this table were applied to the emission rates quoted in this section to obtain the emission rates of particular size fractions.

Table 4.2 Particulate Matter Emission Factors from IDI Diesel Car Without Catalyst (Regulation ECE 15.04 (83/351/EEC)) - g/km.

Road Type	**Engine Temperature**	**Engine Size**		
		Small (<1.4 l)	Medium (1.4-2 l)	Large (> 2 l)
Urban	Cold	0.24	0.34	0.36
Urban	Hot	0.12	0.17	0.18
Minor Rural	Hot	0.10	0.13	0.15
Major Rural	Hot	0.09	0.11	0.13
Motorway	Hot	0.15	0.20	0.22

PM_{10} emission rates for existing vehicles are those detailed in *UK Petrol and Diesel Demand* (Gover et al, 1994) which result from a detailed survey of the literature. The most detailed information is available for diesel cars and Table 4.2 shows the average emission rates of particulate matter on different types of road.

Less is known about emissions from other diesel vehicles, such as buses and coaches. Far fewer measurements have been made on large vehicles and some of these factors, especially for buses, have been estimated on the basis of measurements made on vehicles with similar engines and a few direct measurements. Table 4.3 shows the factors for other diesel vehicles.

There is little available data for petrol engine emissions of particulate matter. The factors in Table 4.4 are the result of a literature survey (Gover et al, 1994; USEPA, 1985) which included some US data which showed the highest mass emission rates for old petrol engined vehicles with leaded gasoline. The range indicates that found in the literature.

Emission limits for particulate matter mass from diesel vehicles will fall in the future due to a series of European Union Directives (91/542/EEC, 94/12/EEC, 93/59/EEC). Table 4.5 indicates the reductions in the

Table 4.3 Particulate Matter Emission Factors for Diesel Road Vehicles- g/km (as PM_{10}).

		Road Type			
		Urban	**Minor Rural**	**Major Rural**	**Motorway**
LGV	IDI non-catalyst	0.28	0.23	0.21	0.29
Small HGV	3.5 - 7.5 t GVW	1.90	1.17		0.83
Medium HGV	7.5 - 17 t GVW	1.53	0.95		1.08
Large HGV	17 - 38 t GVW	1.52	0.91		0.71
Mini-bus	up to 16 seats	0.40	0.36		
Midi-bus	17-35 seats	1.90	1.17		
Bus	over 35 seats	1.60	1.40		
Coach	over 35 seats	1.52	0.91		0.71

Table 4.4 Emission Factors for Total Particulate Matter from Petrol Engined Vehicles - g/km (as PM_{10}).

	Emissions	**Range**
Car non-catalyst leaded	0.06	0.02 - 0.16
Car non-catalyst unleaded	0.02	0.02 - 0.03
Car three-way catalyst	0.01	0.01 - 0.02
LGV non-catalyst leaded	0.08	0.05 - 0.11
LGV non-catalyst unleaded	0.04	0.03 - 0.05
LGV three-way catalyst	0.02	na

emission rates implied by these Directives. These are based on the Directive test values assuming that on-road emissions are at the maximum levels specified by the Directives, and hence the actual emission rates may be different in practice.

The introduction of unleaded petrol and three-way catalysts has resulted in a decrease in the emission rates of particles from petrol engines but this reduction was not the result of a specific particulate emission limit regulation. Emissions reduced with the introduction of unleaded fuel, and a further reduction with the use of three-way catalysts was the result of emission limits for NO_x, VOC and CO.

Data on particulate matter emissions from large diesel engines, trucks, buses and coaches are sparse. In particular the contribution of these vehicle types in the past is poorly quantified. Often, measurements were made on engine test beds rather than whole vehicles on the road or on a chassis dynamometer. Also, while vehicle emissions may increase as the vehicle ages

Table 4.5 Past and Future Reduction in Regulated Particulate Matter Emission Rates.

Date of introduction	**Petrol with three-way catalyst**	**Diesel Car IDI**	**Diesel LGV**	**HGV <85kW**	**HGV >85kW**
Pre 1993	100	100	100	100	100
31/12/92		56			
1/10/93				46	46
1/10/94			56		
1/1/96		32			
1/10/96				12	19
1/10/97			44*		

Normalised emission rates. Pre-1993 = 100

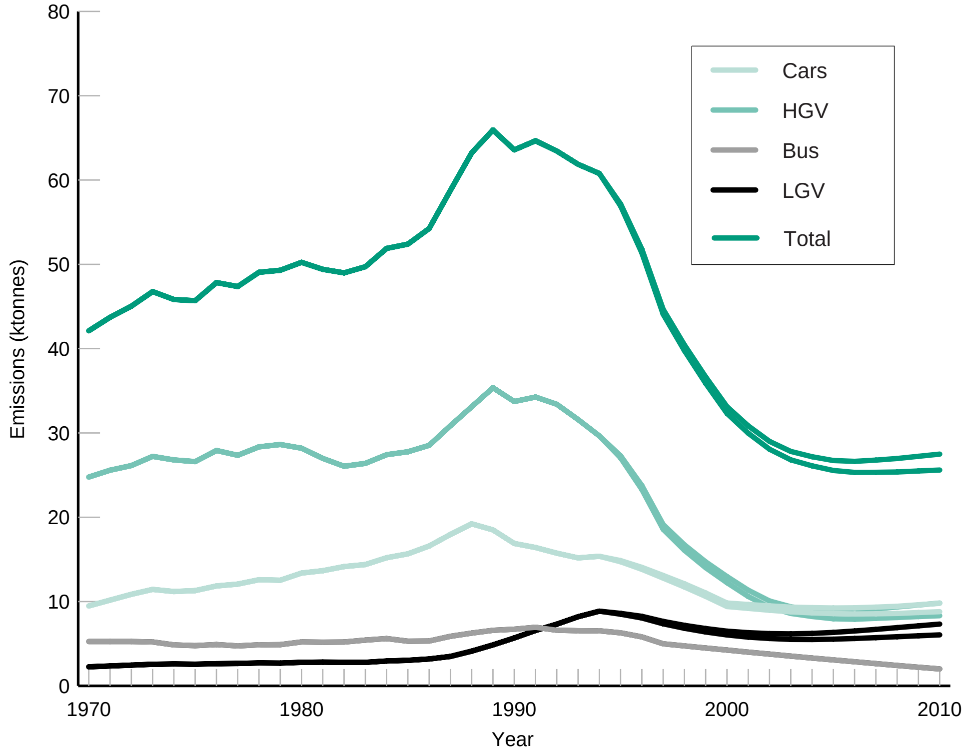
* This is a weighted average as different rates apply to different weight classes

Table 4.6 Exhaust Emissions of PM_{10} from Road Traffic (ktonnes).

		1970	1975	1980	1985	1990	1995	2000	2005	2010	2015	2020	2025
Cars	**Petrol**	9.0	10.7	12.6	14.7	14.8	10.3	4.5	4.1	4.2	4.4	4.7	5.0
	Diesel	0.5	0.6	0.7	1	2.1	4.5	5.1	4.8	5.1	5.7	6.1	6.5
	All Cars	9.5	11.3	13.4	15.7	16.9	14.8	9.6	8.9	9.3	10.1	10.8	11.5
LGV	**Petrol**	1.2	1.4	1.5	1.6	1.4	0.2	0.1	0.1	0.1	0.1	0.2	0.2
	Diesel	1.1	1.2	1.3	1.4	4.3	8.3	6.2	5.8	6.6	7.5	8.5	9.6
	All LGV	2.3	2.6	2.8	3.0	5.7	8.6	6.3	5.9	6.7	7.6	8.6	9.8
HGV	**Large**	3.3	3.8	5.0	5.7	8.2	7.1	3.3	2.2	2.4	2.6	2.9	3.2
	Small	21.5	22.8	23.2	22.1	25.5	20.1	9.3	6.2	6.7	7.4	8.2	9.1
	All HGV	24.8	26.6	28.2	27.8	33.7	27.2	12.6	8.4	9.1	10.0	11.1	12.2
Buses and Coaches		5.3	4.8	5.2	5.3	6.7	6.3	4.2	3.1	2.0	1.4	1.3	1.3
Motorcycles		0.4	0.4	0.7	0.6	0.6	0.4	0.4	0.4	0.4	0.5	0.5	0.5
All Diesel		31.6	33.2	35.4	35.5	46.8	46.3	28.1	22.1	22.8	24.6	26.9	29.7
All Petrol		10.6	12.5	14.8	16.9	16.7	10.9	5.0	4.6	4.7	5.0	5.4	5.7
Total		**42.1**	**45.7**	**50.2**	**52.4**	**63.6**	**57.2**	**33.1**	**26.8**	**27.5**	**29.6**	**32.3**	**35.4**

Note: Assumes diesels comprise 20% of new car sales.

Figure 4.3 UK Road Transport Emissions of PM_{10} (Diesel Car Sales 20%).



Note: The split lines in future projections correspond to low and high forecasts of traffic.

this has not been well quantified. In the figures quoted in this Chapter any effect of vehicle wear and tear has not been included.

Table 4.6 and Figure 4.3 show the emission estimates that result from these emission factors. The future vehicle usage assumed in the calculation is the mean of the upper and lower projections from the Department of Transport's National Road Traffic Forecasts (these are predictions of road traffic up to

2025). The introduction of low sulphur diesel in 1996 will reduce particulate matter emissions from existing diesel engines by up to 13% for HGV and have a smaller, but beneficial effect upon emissions from light duty vehicles. Diesel cars are assumed to comprise 20% of new car sales, close to the percentage achieved in 1994/95.

4.2.2 *Road Transport - Other Emissions*

Particulate matter is also emitted from tyre wear and brake wear. Information from the USA gives an indication of the importance of these sources.

4.2.2.1 *Tyre Wear*

The USEPA gives a factor of 0.002 g/mile for particles <10µm (0.0012 g/km) for tyre wear from cars. As the particles are produced by attrition processes, particle sizes are probably larger than for exhaust emissions, and so emissions of particles less than 2.5µm are likely to be negligible. Assuming that HGVs have larger emission rates (scaling as the number of wheels) and that these figures apply to the UK this gives the emission rates shown in Table 4.7.

4.2.2.2 *Brake Linings*

The USEPA gives a factor of 0.0128 g/mile (0.00795 g/km) of particles from wear of brake linings on cars. Table 4.1 shows that 98% of these emissions are less than 10µm. Again, assuming that emissions from large vehicles are larger than from cars (emissions are scaled according to the number of wheels) and that these US figures apply to the UK, emission estimates appear in table 4.8.

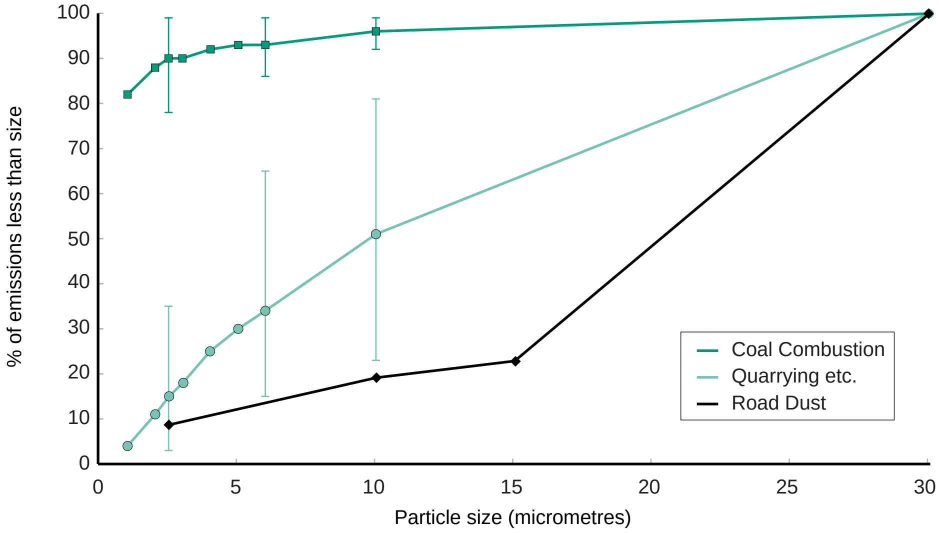
Table 4.7 Annual Tyre Wear Emissions of PM_{10} (ktonnes) in the UK.

	1970	1980	1990	1993
Tyre Wear Emissions (ktonne)	0.31	0.39	0.57	0.57

Table 4.8 Annual Brake Wear Emissions of PM_{10} (ktonnes) in the UK.

	1970	1980	1990	1993
Brake Wear Emissions (ktonne)	1.95	2.61	3.78	3.80

Figure 4.4 Typical Cumulative Particle Size Distributions for Particles from Coal Combustion, Quarrying and Road Dust (USEPA, 1990).



Note: Error ranges are 95% confidence intervals.

4.2.2.3 Road Dusts

Particulate matter may also enter the atmosphere from dust on the road surface. This dust is entrained by the motion of the vehicle along the road. It may come originally from deposited atmospheric dusts, material carried onto the road by vehicles or erosion, or the wear of the road surface itself.

It is very difficult to estimate the emission from these sources. The USEPA has produced a formula which is appropriate for the USA, but notably not for the much wetter climate of the UK. The US data does give an indication of the particle size distribution for these sources. Of the TSP emitted about 20% is PM_{10} and less than 9% $PM_{2.5}$ (see Figure 4.4).

One of the factors that determines the emission rate is the ‘silt loading’ of the road. This is the mass of ‘silt’, defined as material less than 75µm, in a square metre of road surface. The USEPA gives a range of silt loadings measured in the US ranging from 0.01 to 30 grams/m^2. There is little information for the UK but Ball and Caswell (1983) give data that would equate to about 0.02 grams/m^2 as an upper limit. This would result in an emission factor for PM_{10} about the same as that for exhaust emissions from petrol engined cars with three-way catalysts. However, as the wet climate in the UK is so different to that of the USA, it is likely that the true annual average emission rate is even lower.

Given the wide range of silt loadings for the USA, and the differences between the UK and USA the annual emission from road dusts in the UK cannot be estimated with any reliability. This is an area that needs further investigation in order to quantify this source.

4.2.3 Other Mobile Sources

4.2.3.1 Railways, Shipping and Aircraft

Emissions from these sources have been estimated from fuel related emission factors. They do not account for significant emissions on a national scale but may be important locally. The current emissions are about 5 ktonnes annually.

4.2.3.2 Off-Road Sources

This is a wide-ranging category than includes a variety of domestic commercial, agricultural and forestry sources, such as lawnmowers, construction plant, cement mixers, chain saws and combine harvesters. A survey of quantity and usage of these sources has is been performed (Precision Research, 1995), and indicates that the current emissionof PM_{10} from these engines is about 2 ktonnes annually.

4.2.4 Other Stationary Sources

4.2.4.1 Domestic Sources

The main source of PM_{10} from domestic premises is from the use of coal. Much of this coal is burnt in open fires with high emissions. Following the smogs of the 1950s and 60s, smoke control areas were introduced, and only "smokeless" fuels can be used in open fires in most urban areas. Over the past few decades there has also been a substantial switch to electricity and gas for domestic heating over much of the UK.

Domestic emissions, whilst they currently amount to 19% of the total UK emissions, are not so important in most urban areas. They may be significant in those small towns and villages where coal and other solid

Table 4.9 Annual Emissions of PM_{10} from UK Power Stations.

	Fuel Burnt ktonnes	Ash Emitted ktonnes	TSP Emission Factor g/kg	% PM_{10}	PM_{10} Emission Factor g/kg	PM_{10} Emission ktonnes	kg PM_{10} Emission per MWh generated
Coal-fired	64,090	64.8	1	80	0.6	38.45	0.267
Oil-fired	4,330	4.8	1.1	20	0.2	0.962	0.116
Gas Turbines	4,556				0.02	0.093	0.004

fuels are still widely used, and in Northern Ireland where no supplies of natural gas are yet available.

4.2.4.2 *Large Combustion Sources*

Power stations are the largest users of coal in the UK. However all coal-fired stations are equipped with electrostatic precipitators (ESP) which remove on average 99.5% of the particulate matter. In contrast, oil fired power stations are not equipped with precipitators. As data on particulate matter emissions from power stations for the whole UK was not available, data for England and Wales (PowerGen, 1994, National Power, 1995) has been scaled up to estimate UK emissions, as shown in Table 4.9. The ash emitted equates to total particulate matter. An increasing proportion of electricity is being generated by plant which uses natural gas as the fuel. The gas emission factor used is the emission limit for an individual gas turbine, which, in fact relates to PM_5 (particulate matter less than 5 microns). While the actual emission of PM_5 will be less than this upper limit, the PM_{10} emission rate is higher than that of PM_5 so the factor was used unchanged to indicate the likely emissions. The final column shows the emissions per MWh generated. This clearly shows how even without ESPs oil-fired stations are cleaner than coal-fired ones with ESPs, while gas-fired station emissions are extremely small.

Other industrial and commercial users use coal in a range of boilers. However these are more efficient than domestic open fires and have lower intrinsic emission rates. Industrial, commercial and institutional users have switched away from coal, initially to oil and now to natural gas. This has steadily reduced emissions. Emissions factors are taken from Gillham et al (1994).

4.2.4.3 *Other Sources*

There are a number of processes that emit particulate matter. These cover a wide range of sources and are difficult to quantify without precise details of the individual emitter.

HMIP has set up a Chemical Release Inventory (CRI) that will include details of the emissions from each authorised site under Part A of the Environmental Protection Act (1990). The emissions included are only for those sites that have been authorised, some sectors still await the authorisation procedure. Also, Part B processes, which come under local authority control are not included. The figures relate to emissions of particulate matter (not PM_{10}) and may include emissions from fuel combustion. They only include emissions after the date of authorisation - there is no indication where the data relate to part of a year. Despite these limitations, the data give valuable insights, but these sources are unlikely to contribute much to urban emissions because of their locations. Table 4.10 lists the particulate matter emissions in the CRI.

Table 4.10 Total Particulate Matter Emissions in the Chemical Release Inventory (tonnes).

Carbonisation and associated processes	626
Gasification and associated processes	55
Petroleum processes	1614
Iron and steel	3
Non-ferrous metals	0.1
Cement/Lime manufacture	4456
Ceramic production	723
Glass manufacture and production	112
Other mineral fibres	536
Asbestos processes	11
Acid processes	8473
Chemical fertiliser production	132
Inorganic chemical processes	347
Manufacture and use of organic chemicals	511
Pesticide production	1
Petrochemical processes	21
Processes involving halogens	88
Incineration	2031
Production of fuel from waste	5
Recovery Processes	18
Total	19764

Estimates of emissions from these process sources can also be made from average emission factors and overall production statistics. The factors were those in the USEPA Factor Information and Retrieval (FIRE) system (USEPA, 1995b). This gives a total of about 30 ktonnes from industrial processes and about 29 ktonnes from sand and gravel extraction and quarrying from stone. This appears to be compatible with the

CRI which is not yet complete and only includes authorised processes. The data from the average factors was used to estimate national emissions, rather than the CRI.

4.2.5 Construction Sources

The amount of dust emissions from a construction site will depend on the size of the site and the amount of construction activity. It would be expected that a component of the emissions would be correlated with the silt content of the soil (the fraction < 70µm) and the speed and weight of the vehicles but negatively correlated with the moisture content of the soil. Other activities on such sites also generate dust.

An American study of TSP around apartment and shopping centre construction sites suggested a factor of 2.69 tonnes/hectare/month. PM_{10} emissions will be lower. Using an estimate that 20% of TSP is PM_{10} gives a factor of 0.538 tonnes/ha/month. (This proportion of 20% comes from data for emissions of dust from roads but is the best estimate available. Given the nature of the source it is likely that the majority of the dust emissions are greater in size that 10µm.) However this data is appropriate to a generally dryer climate and the emissions in the UK should be lower.

Material carried outside the site and deposited on nearby roads may be entrained either by passing traffic or the wind and may result in a significant source. The US factors are not appropriate for the UK as they depend on a dryer climate. The damper conditions in the UK result in much lower emissions. Currently these do not appear to be significant on a UK scale but they may be important locally.

Despite these problems with the data an order of magnitude estimate is possible. The amount of construction in the UK annually includes 150,000 to 200,000 houses, 2 to 2.5 million m^2 of office floorspace, 11.5 to 12.5 million m^2 of industrial and warehousing floorspace and 1.5 to 2 million m^2 of retail floorspace (DoE 1992, 1994). Assumptions need to be made to account for the greater area developed than the actual floorspace, the length of time building takes, and a reduction for the amount of rain in the UK. The number of days with rain each year is about 150 to 250 (as measured by the Department of the Environment’s acid rain monitoring network) (Hjellbrekke et al, 1995). Therefore the emissions should be no more than one half of those in an arid climate. All these factors lead to an estimate of 0.5 - 8.3 ktonnes of PM_{10} annually.

In order to check this, these emissions can be compared with emission rates for other similar processes. The total amount of waste arising from these activities in the UK is about 70 million tonnes (DoE, 1995). Of this, about 24 million tonnes is brick and concrete with most of the remainder soils and clays. An emission of 0.5 - 8.3 ktonnes annually would indicate an emission rate for construction and demolition of 0.007 to 0.119 kg/tonne of waste produced. US emission factors for mineral handling, quarrying and mining range from 0.001 to 54 kg/tonne (USEPA, 1995a) and so the emission rate estimate for demolition and construction seems to be a reasonable estimate considering that the damper conditions in the UK should reduce emissions below US levels.

The local effects of construction work can be seen in ambient measurements. During 1994 the monitoring site in Cardiff showed elevated levels (up to 80% higher monthly mean) from June to October. This is thought to be due to construction work which started in January and finished in October. The reduced impact of the work during January to May could be due to both the nature of the work and the weather. In winter and spring it will both rain more and dry slower; this will reduce emissions.

4.2.6 Agricultural

Emissions from agricultural activities can potentially come from a range of activities. These include land preparation, fertiliser application and harvesting. Stubble burning is now, except for a few limited exceptions, banned in England and Wales so this is no longer a significant source.

Of the different sources it is expected that harvesting is the main source if only because it is usually done when the crops are dry and so conditions will be suitable for larger emissions. Currently, suitable

Table 4.11 UK Emissions of PM_{10} (ktonnes).

	Source	1970	1980	1990	1991	1992	1993	1993 as %
1	**Public power etc**	41	58	39	39	39	40	15%
	Coal	38	57	38	38	38	38	14%
	Fuel Oil	3	1	1	1	1	1	0%
	Other	0	0	0	0	0	0	0%
2	**Commercial Institutional & Residential Combustion Plants**	226	96	45	47	45	42	16%
	Domestic	210	88	39	41	37	37	14%
	Other	16	9	6	5	5	5	2%
3	**Industrial Combustion Plants & Processes with Combustion**	131	60	46	45	44	44	17%
	Refineries	10	10	6	6	6	7	3%
	Iron and Steel	56	17	21	21	20	20	8%
	Other	65	33	19	19	18	18	7%
4	**Non-Combustion Processes**	63	63	63	63	63	63	24%
	Construction	4	4	4	4	4	4	2%
	Industrial Processes	30	30	30	30	30	30	11%
	Mining and Quarrying	29	29	29	29	29	29	11%
5	**Extraction & Distribution of Fossil Fuels**	0	0	0	0	0	0	0%
6	**Solvent Use**	0	0	0	0	0	0	0%
7	**Road Transport**	44	53	68	69	68	66	25%
	Petrol Exhaust	11	15	17	16	14	13	5%
	Diesel Exhaust	32	35	47	49	50	49	19%
	Non-exhaust (Tyres and Brakes)	2.3	3	4.4	4.4	4.4	4.4	2%
8	**Other Transport**	20	9	7	7	7	7	3%
9	**Waste Treatment & Disposal**	0	0	0	0	0	0	0%
10	**Agriculture**	2	1	1	1	1	1	0%
11	**Nature**	0	0	0	0	0	0	0%
	TOTAL	**527**	**340**	**269**	**271**	**267**	**263**	**100%**

emission rates have not been found to estimate this source. It is likely to be very seasonal and to only have a local impact in rural areas.

4.3 EMISSION ESTIMATES

4.3.1 National Emission Estimates

Table 4.11 shows estimated emissions of PM_{10} from all sources. The sources are grouped into eleven sectors. These are the standard source sectors used internationally by the UNECE and the EU to describe and compare emissions.

These estimates are the best that are currently available. However, as was discussed above, there are considerable uncertainties in some of these figures. The emissions in 1970 may have been higher as emission rates for road transport may have been higher in those years. No time trend for group 4 (non combustion processes) has been attempted due to those uncertainties.

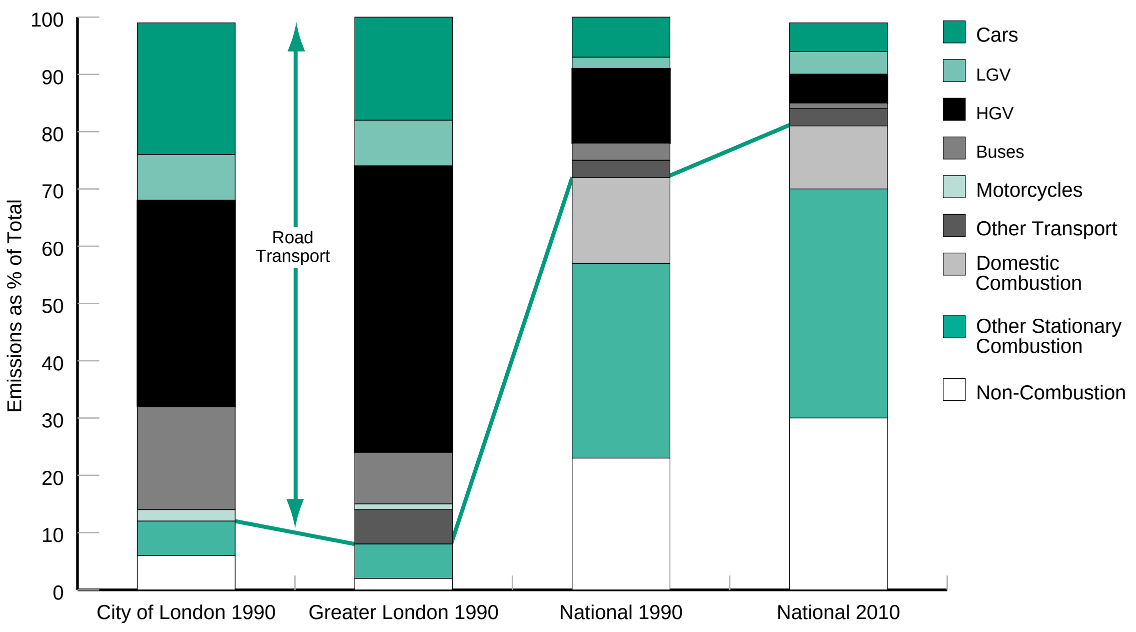
These are national emissions. In urban areas the picture will be very different, as some of the sources do not occur in populated urban areas. For example, the domestic emissions are almost entirely from coal use, which is subject to severe restrictions in most urban areas which are subject to smoke control.

Table 4.12 Emissions of PM_{10} in London in 1990.

	Emissions (tonnes)		Emissions as %	
	City of London	**Greater London**	**1x1 km***	**Greater London**
Cars	14	1430	13%	16%
Taxis	11	182	10%	2%
LGV	9	699	8%	8%
MGV	31	2508	28%	28%
HGV	9	1968	8%	22%
Buses	20	766	18%	9%
Motorcycles	2	75	2%	1%
Trains	0	16	0%	0%
Water	0	5	0%	0%
Air	0	558	0%	6%
Domestic	0	12	0%	0%
Industrial	1	212	1%	2%
Commercial & Institutional	6	325	6%	4%
Construction	7	220	6%	2%
TOTAL	111	8975		

* Equates approximately to the City of London.

Figure 4.5 Comparison of London and UK Emissions of PM_{10}.



Industrial emissions do not usually occur in central urban areas. In the London area there is only one large coal user left, and that is on the periphery of the urban area. The main source nationally of PM_{10} from stationary fuel use is from the burning of coal.

Figure 4.6 Monthly Mean Concentrations of PM_{10} for Urban Background Sites, 1993 and 1994.

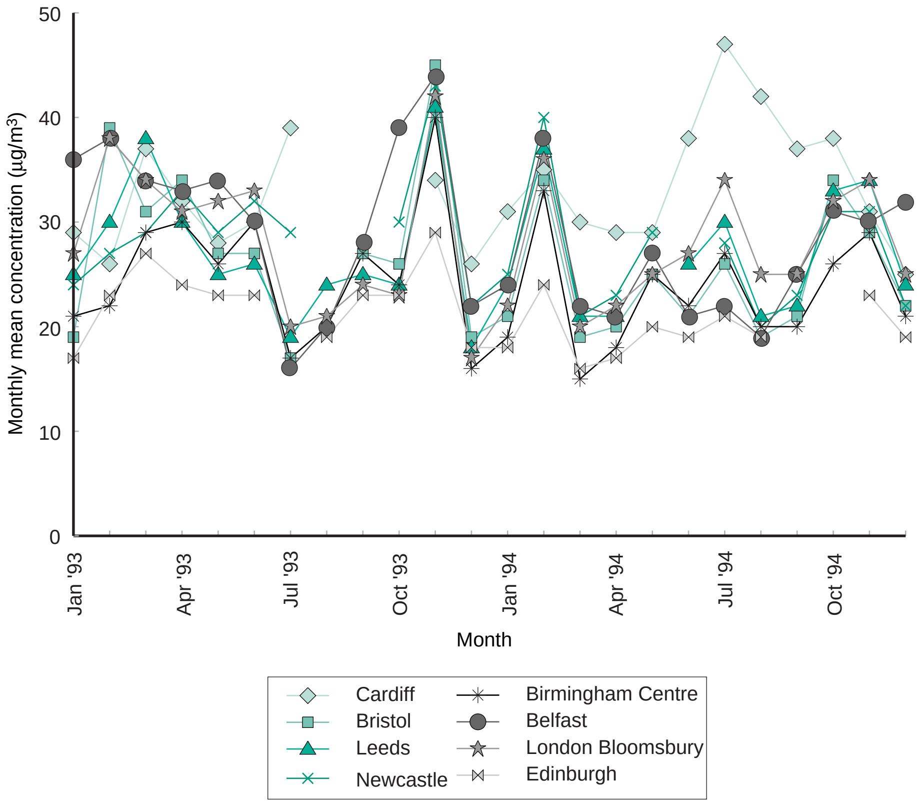
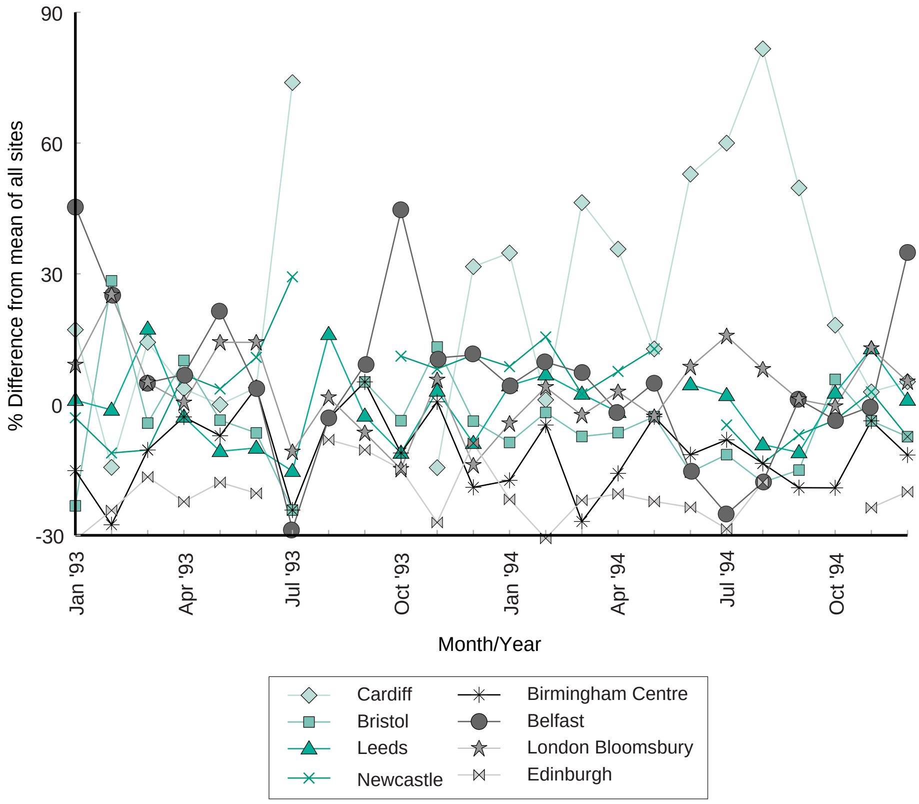


Figure 4.7 PM_{10} Monthly Means - % Deviation from Mean of all Sites.



These figures show that on a national scale road transport accounts for about one third of the emissions. About a half comes from stationary fuel combustion.

4.3.2 *PM$_{10}$ Emissions in London*

Emissions in urban areas will differ substantially from national emission estimates. Sources such as domestic and industrial fuel use will be much reduced while road transport will become a much more important source.

An inventory of emissions from energy-related sources for London has been made for 1990 on a 1x1 kilometre grid (LRC, 1993). It covered an area broadly similar to the extent of the old Greater London Council. This considered a number of pollutants but not PM$_{10}$. However, as the emission factors that were used in it are known it is possible to make an estimate of the emissions of PM$_{10}$ in London based on their estimates of black smoke. Estimates of emissions from construction were added, scaled from the national estimates based on the employment in construction work in London and the UK. The other sources, such as mining and quarrying, do not occur significantly in the area covered by this London inventory, shown in Table 4.12.

Figure 4.5 compares emission estimates for Greater London with national emission estimates. This clearly shows the predominance of road transport emissions of particulate matter in London. The national 2010 estimates are discussed in Section 4.5

4.4 AMBIENT PM$_{10}$ LEVELS AND EMISSIONS

Ambient concentrations of PM$_{10}$ are measured at a number of sites across the UK; the measurement methods and data are described in Chapter 6. There is some interesting information about emissions that can be extracted from the measurements.

Eight sites produced data for both 1993 and 1994 and are considered here. All the sites are classified as urban background. The emission data described above implies that most of the PM$_{10}$ emissions in the area around the sites would be from road transport, which does not have a significant seasonal variation.

The exceptions to this are Belfast and Cardiff. Belfast has no natural gas supplies, and as a result

Figure 4.8 Past and Projected UK Urban Road Transport Emissions of PM$_{10}$ (Diesel Car Sales 20%).

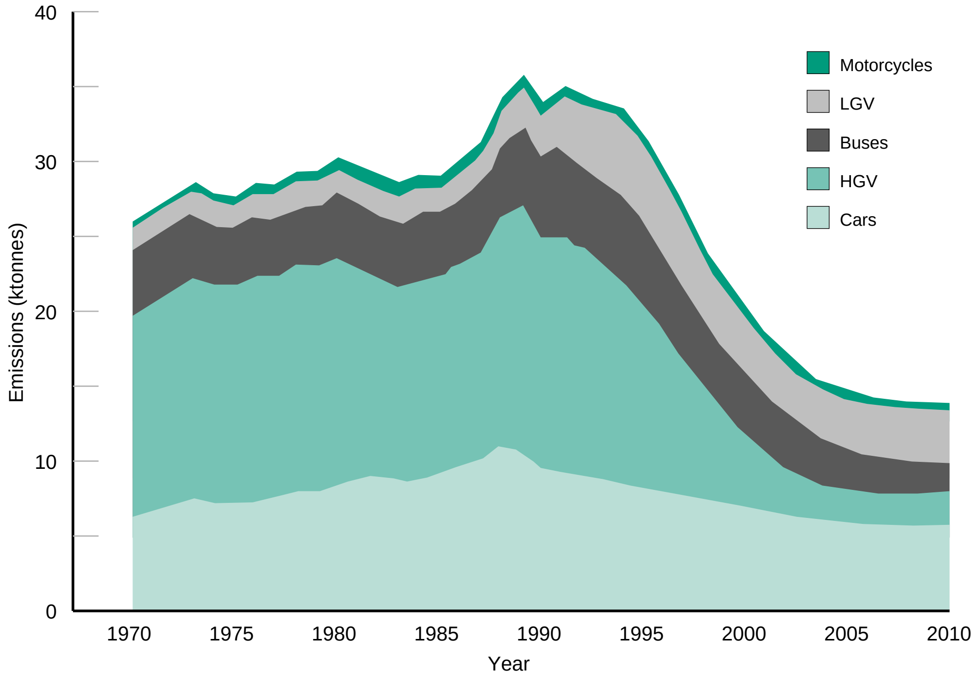
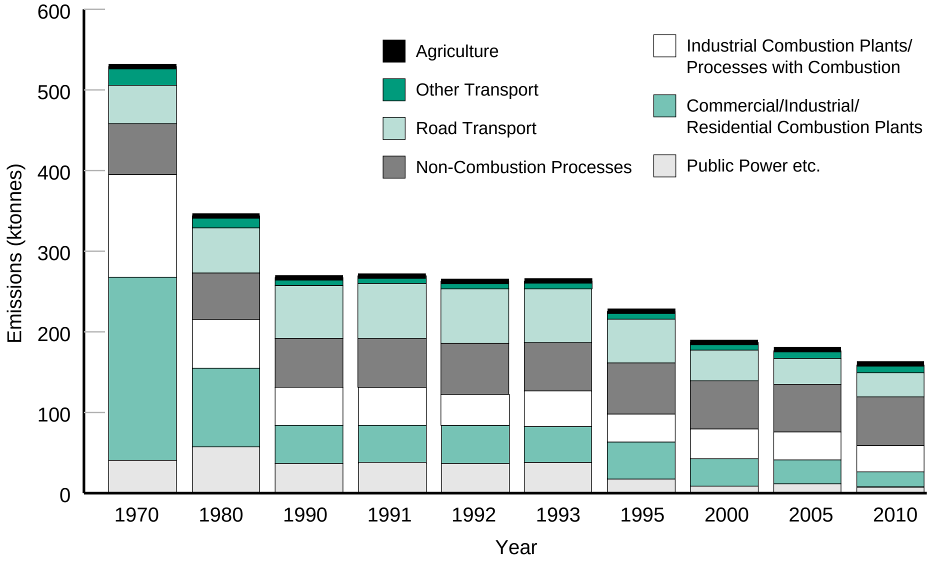


Figure 4.9 UK Emissions of PM_{10} by Source Category, 1970-2010.



there is still considerable domestic coal combustion. Thus, there should be a seasonal contribution to the winter PM_{10} emissions as coal burning occurs predominantly in the winter. The Cardiff site was very close to construction work which started in January 1994 and lasted until October 1994.

Figure 4.6 shows the monthly mean PM_{10} concentrations for the sites. Two features are particularly notable. Firstly the Cardiff site does not follow the same pattern as the other sites, particularly in the central 10 months or so of 1994. Secondly, it is striking how the concentrations at all the sites rise and fall together. Weather conditions are one factor that drives this, with still, stable conditions leading to elevated concentrations. Figure 4.7 presents the same data in a different way. The mean concentration for all the sites was calculated. Then, for each site, the percentage difference from this overall mean was plotted. This shows that, except for two sites, all the monthly mean concentrations are within ±30% of the mean. The exceptions are Cardiff and Belfast. The elevated levels at Cardiff seem to have stopped in October 1994, when the construction work ended. The cause of the peak in July 1993 is not known. The elevated levels in Belfast occur in the winter months while in the summer the concentrations are lower than the UK mean.

These results are consistent with our knowledge of PM_{10} sources. A local construction source has a large impact on the air quality with an increase of nearly 90% in one monthly mean and an increase of over 50% for six months. This would imply that over a third and up to a half of the ambient PM_{10} concentrations at Cardiff during January to October 1994 were caused by the construction work. In Belfast the concentrations are about 40% higher than the overall mean in the winter and up to 30% lower in the summer. This indicates that of the order of a half of the monthly mean ambient PM_{10} concentrations are coming from domestic smoke in the winter.

The other sites show much similarity in behaviour to one another and thus are likely to have similar sources. More detailed analyses of ambient data are presented in Chapter 6, and receptor modelling in Chapter 8.

4.5 FUTURE EMISSION TRENDS

Predicting future trends in emissions of PM_{10} relies on making judgements and assumptions on future activities, both nationally and in urban areas. The emissions estimates presented here are based on the following assumptions:

Table 4.13 - PM_{10} Sources in Order of Decreasing Reliability of Emission Estimate.

Source	Comments
Diesel Cars	Based on a number of detailed measurements
Diesel LGV and HGV	Based on a few measurements
Diesel Buses and Coaches	Only a few measurements. For some types the factors are extrapolated from similar vehicle types.
Petrol Cars	Only a few measurements. The factors chosen are uncertain especially for cars without catalysts
Other Mobile Sources	Little data and uncertain activity data.
Stationary Combustion	Only a few measurements. Some of the PM_{10} factors have to be interpreted from smoke or TSP data
Industrial Processes	Few data of questionable applicability. Order of magnitude estimates possible.
Mining and Quarrying	Few data of questionable applicability. Order of magnitude estimates possible.
Construction	Only USA data which is not strictly appropriate for the UK. Order of magnitude estimates possible.

- In the absence of any other information it is assumed that emissions from non-fuel combustion stationary sources will continue into the future at their current rates. Changes in PM_{10} into the future will depend primarily on changes in two sectors; fuel combustion and road transport.

- Road transport emissions of PM_{10} will change as result of two factors: increasing road usage and the implementation of stricter emission limits on new vehicles. The National Road Transport Forecasts (NRTF, DoT, 1994) have been used as the basis of predictions of the growth of vehicle kilometres and vehicle fleets.

- Future European emissions regulations that have already been agreed to are included. Limits for HGVs come into force in 1995/6 (91/542/EEC). New car limits will come into force in 1996 (94/12/EEC) while limits on diesel vans will come into force in 1997 (93/59/EEC). New, Stage III limits for emissions from vehicles are planned to be introduced by the EU in 2000. These are, however, still the subject of discussion and cannot be included in the projections. It is assumed that diesel cars will account for 20% of all car sales each year from 1995.

The make-up of the vehicle parc, and in particular the percentage of diesel vehicles in the car fleet is an important determinant of the emissions from road transport. In our Second Report (QUARG, 1993), this Review Group showed that future reductions in particulate matter emissions effected by tighter exhaust emission regulations could be largely lost if the percentage of diesels in the car fleet approached 50% as in some other European countries. Hence the predictions are highly sensitive to the market share of diesel cars.

Figure 4.3 shows the latest projection of road transport emissions of PM_{10} in the UK, whilst Figure 4.8 shows the road transport emissions in urban areas only. As this follows the NRTF, it may overestimate emissions for London, where traffic growth is now well below the national average. Emission estimates for stationary fuel use are based on estimates of fuel use published by the DTI (DTI, 1995). The scenario based on 'central growth, low fuel prices' (DTI, 1995) is used. While the amounts of fuel used change, specific emission rates are assumed to be constant. Figure 4.9 shows national emission estimates until 2010.

Estimates of future emissions in urban areas depend on the traffic growth estimates for those urban areas. Such estimates are not currently published, and each urban area is likely to be different. However, it is clear that road transport will continue to be dominant in urban areas until after 2010.

4.6 UNCERTAINTIES

Emission inventories are estimates of emissions of specific pollutants from a given area over a specified time period. While measured data is used where possible, it is also necessary to include estimates of emissions from some categories of source because it is impossible to measure all the sources all the time. Additionally it cannot be stated with certainty that all the sources that exist have been considered. In practice, the major sources are included as they are well known and any ‘missing’ emissions are small.

The estimates are generally based on a few measurements with the assumption that these results are typical of the behaviour of all similar sources.

The emission estimates of PM_{10} presented in this Report are based where possible on measurements of PM_{10} emissions, although in some instances measured total particulate matter emissions have been converted to PM_{10}. While there have been a number of investigations of particulate mass emission from diesel-engined motor vehicles, this is not true of many fugitive sources. Stationary fuel combustion falls between these extremes. The figures presented above are indicative estimates only for some sources, particularly construction, quarrying and industrial processes. Given the lack of knowledge about these emissions it is not possible to give quantitative indications of the accuracy of the emission estimates. It is however possible to give an indication of the reliability of the estimates, and these are presented in Table 4.13.

A joint research programme sponsored by the Department of the Environment, Department of Transport and the motor industry is currently investigating size-fractionated mass and number emissions of particles from petrol and diesel vehicles, and should enable more accurate estimates of emissions from road vehicles to be made in the future.

4.7 BIOLOGICAL PARTICLES

The biological content of airborne particulate matter has been an important area of scientific interest since the nineteenth century. Transmission of hospital infections and pathogenic crop diseases are known to be related to the varied airborne dispersal mechanisms of micro-organisms, and considerable research has been undertaken within these fields.

The biological particles present in ambient air, including pollen grains, fungal spores, bacteria and viruses, have all been implicated in a wide variety of health issues. Clearly, allergenic response to certain pollen species presents an annual misery for millions of hayfever sufferers across Europe. Also, occupational diseases such as Farmer's Lung and Toxic Organic Dust Syndrome are known to be related to extended exposure to high concentrations of fungal spores found in certain working environments. Direct infection by such organisms as Legionella bacteria from air conditioned buildings has also held a high media profile, although with respect to a relatively small number of cases. High episodic levels of spores released by heavy summer rain have been related to ten fold increases in asthma admissions (Packe and Ayres, 1986). Although the significance of natural allergens for asthmatics has been well documented, little is currently known of the relative mass composition of the species-specific or general biological aerosol with respect to the detailed determination of urban PM_{10} concentrations.

Table 4.14 Atmospheric Micro-organisms and their Relative Sizes

Micro-organism Type	Mean size (µm)
Pollens	10-100
Fungal Spores	5-40
Bacterial Spores	0.3-20
Viruses	0.003-0.5

Biological components associated with airborne particulates have historically been assessed by traditional microbiological growth techniques (agar plates) or by optical (microscope) analysis. The typical sizes of different types of micro-organism appear in Table 4.14. Many sampling techniques are now understood to be far from quantitative, and in addition, many detection methods are significantly biased towards some organisms and against others. This lack of qualitative and quantitative information suggests data from past research is often not representative of the real environment, nor easily comparable to other research. Data on the sources and variability of bioaerosols in the atmosphere will therefore be dependent upon these sampling and analytical issues. In addition, the biological viability of any given species in the atmosphere will depend upon its tolerance of UV radiation, relative humidity and temperature fluctuations, although the importance of the physical aerosol may not necessarily be related to its biological activity.

The terrestrial rather than marine environment is generally considered to be the major source of airborne micro-organisms (Roffey et al, 1977). Vegetation and general farming activities, including animal husbandry and arable cropping are major contributors to the ambient bioaerosol, although release mechanisms will depend strongly on meteorological conditions. Urban sources of bacteria have been estimated to be up to an order of magnitude greater than corresponding rural regions (Bovallius et al, 1978). However seasonal and regional activities, such as wheat harvesting, may reverse the source apportionment of specific species. More easily defined anthropogenic sources include sewage treatment works, landfill sites and power generation cooling towers.

Although variability in composition will depend heavily on seasonal and diurnal cycles, specific species viability and release may be greatly influenced by the relative impact of rainfall, high wind speeds, and fluctuating humidity. Overall it has been suggested that bacteria are associated mostly with springtime, yeasts during the summer, and fungal spores in the winter. Pollens are generally greatest during warmer months, with grasses normally peaking in late June and early July. Tree pollens tend to peak earlier in the spring with Platanus pollens highest in April and Betula during May. Diurnal pollen studies have found maximum release generally occurs during late afternoon (Norris-Hall and Emberlin, 1991). Clearly, variability between differing years may be great, and in addition, as little as 1 mm rainfall will rapidly remove the majority of pollens from the atmosphere, leading to large hourly and daily fluctuations. Qualitatively, bioaerosol composition analysed between 1958 and 1961 in Cardiff found that mean pollen levels represented just 2% by number of the bioaerosol content of the atmosphere (Knox, 1979), the remaining components being made up of bacteria and fungal spores. Other quantitative studies have determined fungal spores peaking at over 50,000/m^3 in July, with lowest recordings around 10,000/m^3 in May. Single bracken fronds have been found to release up to 300 million spores during the late autumn. One determination of pollen release from cultivated grass estimated 210 kg per hectare during the year (Knox, 1979).

With the increased awareness of the importance of airborne particulates, it is perhaps surprising that relatively little is known of the importance or relative mass composition of the biological component of ambient air in relation to the PM$_{10}$ levels routinely measured in urban areas. Ongoing development of molecular DNA techniques may soon be able to provide more reliable qualitative and quantitative data on the biological composition of ambient aerosol. Further assessment of the importance of these parameters can then be considered in relation to other current research into urban air quality and health.

4.8 KEY POINTS

- *Road transport is a significant source of primary particulate matter emissions, especially in urban areas. Nationally it accounts for about a third of emissions of PM$_{10}$; in London this rises to over 80%.*

- *Stationary combustion sources are significant contributors to particulate matter emissions on a national scale. They account for about one half of the PM$_{10}$ emissions. However in cities this contribution may become very small; in London it accounts for about 5% of all the emissions, but is larger in Belfast.*

- *There are a number of industrial processes that can emit large quantities of PM$_{10}$. While this may dominate emissions locally they do not contribute a large fraction of the emissions nationally.Their impact on urban inventories is generally also small due to their being sited out of town.*

- *Primary national emissions of PM$_{10}$ are predicted to fall by about one quarter between 1995 and 2010.*

- *Future emissions of PM_{10} in cities will depend crucially on the amount of diesel fuel consumed and the proportion of diesel vehicles in the fleet.*

- *Emissions estimates for PM_{10} from different source categories vary greatly in their reliability. The most reliable are from diesel cars and are based on a number of detailed measurements. Contributions from some other sources such as mining and quarrying, and construction are subject to great uncertainty.*

- *Biological particles comprising pollens, fungal spores, bacteria and viruses are widespread. Whilst their number concentrations have been evaluated, their contribution to particle mass is not known.*

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5 Sources and Concentrations of Secondary Particulate Matter

5.1 INTRODUCTION TO SECONDARY PARTICULATE MATERIAL

In this section, attention is directed to that fraction of the suspended particulate material in the particle size range of less than 10 micrometres (µm) in diameter, which was not directly emitted into the atmosphere in particle form. A significant fraction of the PM_{10} consists of particles containing material which was originally present in the gas phase in the atmosphere, but has been subsequently taken up into the particulate phase. The term secondary particulate material refers to this material, originally gaseous but present as an intimate component of the PM_{10}.

Reviews of the many thousands of measurements of the particle size distributions of the suspended particulate matter in urban atmospheres have been synthesised to yield idealised relationships between the number of particles, their superficial area, volume and mass, and their particle diameters. Figure 5.1 shows the idealised particle size distribution of urban aerosols in the USA, in the form of three curves showing the number-, area- and volume-size distributions, taken from Whitby (1978).

Figure 5.1a shows the fraction of the number of particles in each size range in the idealised urban aerosol. The curve shows a predominant single peak with a shoulder to higher particle sizes. This number distribution peaks at about 0.013 µm (13 nm) with a total number density of about 100,000 particles/cm^3. Particles in the size range less than 0.1 µm are said to be in the nucleation mode and include the Aitken nuclei.

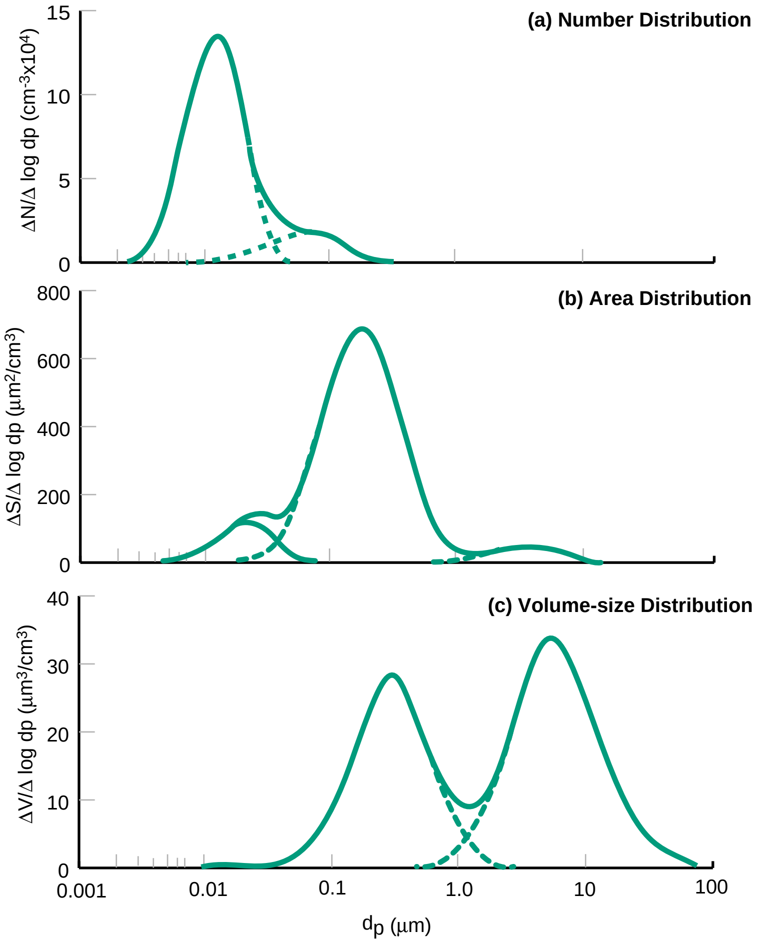
Nucleation mode particles have been emitted into the atmosphere as primary particles by combustion sources (primary particulate material), both stationary and mobile. These particles include elemental carbon from diesel vehicles and flyash from pulverised coal-fired power stations. However, some nucleation mode particles are formed by condensation of gaseous material through gas-particle conversion processes (secondary particulate material). Few vapours can readily form totally new nucleation mode particles directly themselves but sulphuric acid vapour, formed by the photochemical oxidation of sulphur dioxide, exhibits this ability. In urban areas, nucleation mode particles are the most numerous of all the particles.

Figure 5.1b shows the fraction of total surface area of the particles in each size range in the same idealised urban aerosol as Figure 5.1a. In this case the curve shows a strong single peak with shoulders to both higher and lower particles sizes. The area distribution peaks at about 0.1 µm with a total area of about 500 $µm^2$ /cm^3. Particles in the size range 0.1 to 1 µm are said to be in the accumulation mode.

Few accumulation mode particles were actually emitted into the atmosphere in this particle size range. Because this mode contains the bulk of the surface area of the particles, see Figure 5.1b, these particles offer the largest target area for adsorbing other aerosol particles (coagulation) or for adsorbing gaseous material. The process of coagulation reduces the number of particles. The process of adsorption of gaseous material from the atmosphere onto pre-existing nucleation or accumulation mode particles leaves the number of particles unchanged but causes the area, volume and mass of the suspended particulate material to grow rapidly. The accumulation mode is therefore the aging region for all small particles because growth is rapid and loss processes are at a minimum at 0.1-0.3 µm. Thus, particles originally present as nucleation mode particles tend to accumulate in the accumulation mode. Typically there might be about 10,000 particles per cm^3 in the accumulation mode in an urban area. Coarse and nucleation mode particles make a small contribution to the total superficial area of the urban aerosol.

Figure 5.1c shows the fraction of the total volume (and hence mass) of the particles in each size range in the same idealised urban aerosol as Figure 5.1a. In this case the curve shows a bimodal distribution and the complete absence of a shoulder to lower particle sizes. The volume (or mass) distribution peaks at particle sizes of about 0.3 and 6 µm, respectively, with total volumes of about 20 and 30 $µm^3$ /cm^3 under each peak. The volume (or mass) of the urban aerosol appears to be in two modes: the accumulation mode and the coarse mode, with the latter containing particles in the size range 2 µm and above. The

Figure 5.1 Idealised Particle Size Distribution of Urban Aerosols in the USA.



Source: based on Whitby (1978).

nucleation mode particles, although the greatest in number contain a negligible fraction of the aerosol volume and mass.

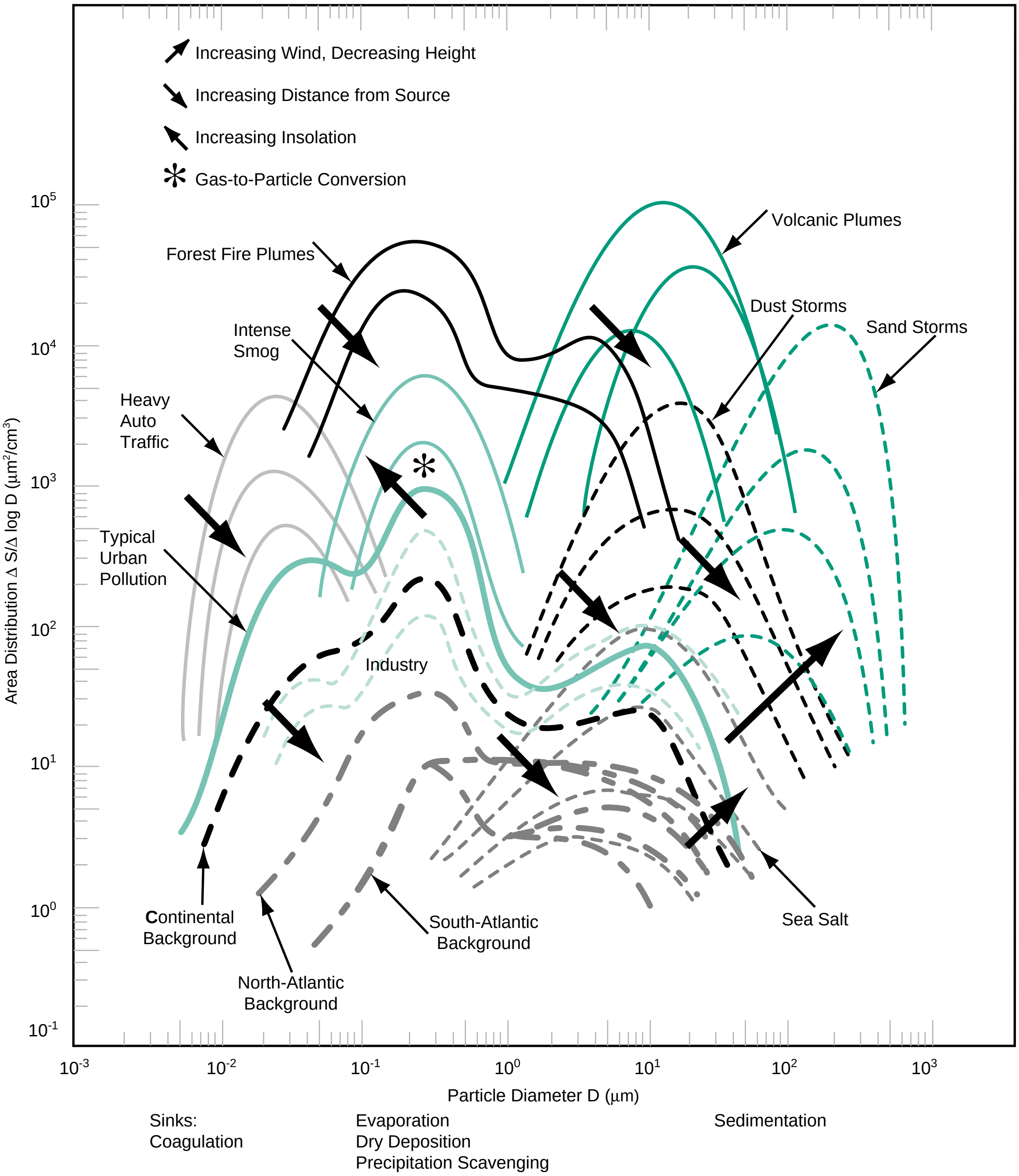
Most of the particles in the coarse mode are formed by the frictional processes of comminution, such as wind-suspended soil dust or evaporated sea-spray (primary suspended particulate material) and from the slow growth of particles from the accumulation mode (secondary particulate material). Typically, there might be a few tens or hundreds particles per cm^3 in the coarse mode in an urban area. However, not all of the coarse mode particles pass through the PM_{10} sampling and monitoring system and are measured. Coarse mode particles account for generally about 20-50% of the urban PM_{10} mass in the UK.

The contributions to the particle size distribution of the different types of atmospheric aerosol are visualised in Figure 5.2, taken from Slinn (1983). Around 1 µm there is a saddle point which separates on the one hand the suspended particulate material formed by storms, the oceans and volcanoes, from the fine particulate matter formed by fires, combustion and chemistry.

Following a consideration of these idealised aerosol distributions, attention is turned to the situation in the United Kingdom and to what is known about the concentrations of secondary particulate material derived from the following sources:

- sulphuric acid and ammonium sulphate in particulate form, derived from the oxidation of sulphur dioxide emitted by combustion sources,

Figure 5.2 Major Sources of Aerosol Particles.



Source: Slinn (1983).

- ammonium and other nitrates in particulate form, derived from the oxidation of nitrogen oxides emitted by combustion sources,

- semi-volatile organic compounds adsorbed onto the atmospheric aerosol, derived from motor vehicles, the resuspension of previously deposited material, industrial processes and stationary fuel combustion,

Clearly, from the definitions adopted here, none of the above sources have been taken into account in producing the emission inventories described elsewhere in this report.

5.2 CONCENTRATIONS OF SECONDARY PARTICULATE MATERIAL IN THE UNITED KINGDOM

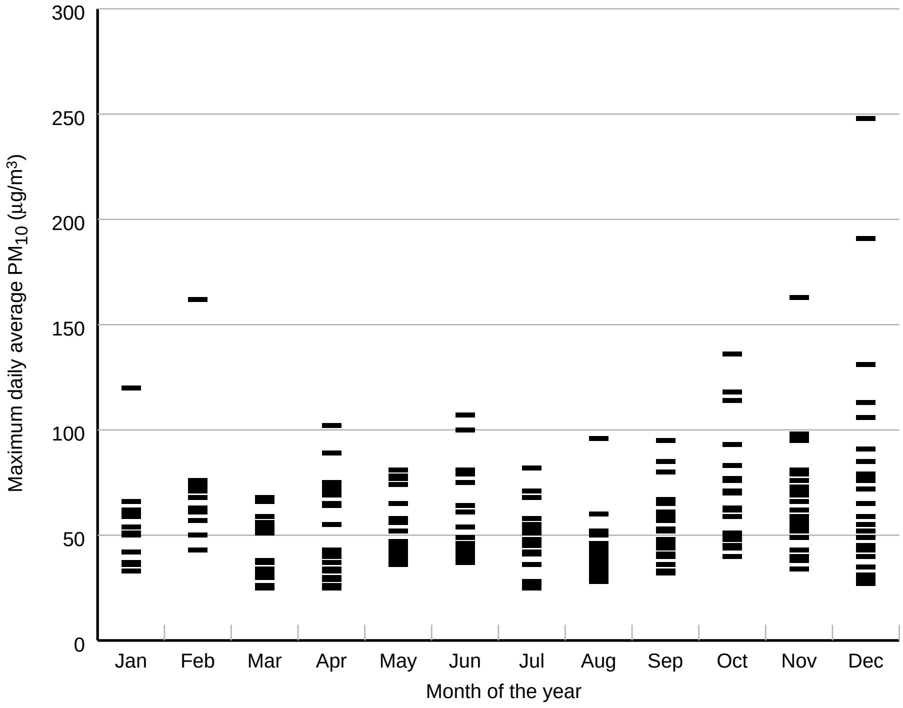
5.2.1 Secondary Particulate Material and the Urban Monitoring Network Data

5.2.1.1 Seasonal Variations in Daily Mean PM$_{10}$ Concentrations

Highest daily mean PM$_{10}$ concentrations in each month (see Figure 5.3) show evidence of substantial seasonal cycles at all the national Automatic Urban Network (AUN) urban background sites. These seasonal cycles are characterised by winter maxima as shown by most urban pollutants. Summertime levels are typically lower than wintertime values. However, relative to wintertime levels, summertime levels do not always fall as low as they do for other primary urban pollutants. This behaviour is usually explained by the presence of a significant summertime source in addition to the wintertime primary source. This additional source is the formation of PM$_{10}$ by the photochemical oxidation of sulphur dioxide and nitrogen oxides.

The primary and secondary contributions to urban PM$_{10}$ levels have different sources, characteristics and spatial scales. The primary contribution tends to be combustion- and traffic-derived and is highly localised in the vicinity of its sources. The secondary contribution is largely sulphuric acid, ammonium sulphate and ammonium nitrate, and is much more evenly distributed, showing little variation across an urban and industrial area. Before further progress can be made towards understanding the impact of present policies on PM$_{10}$ air quality and the significance of the rollback required to meet the air quality standard recommended by EPAQS, there is an important requirement to quantify the relative contributions from primary and secondary sources in the different urban areas and with time of year. This is a large task and one for which we have only preliminary results available, at present. These have largely been obtained by examining the correlation between PM$_{10}$ and traffic pollutants at the AUN sites. The traffic pollutants studied are benzene, carbon monoxide, and NO$_x$, all of

Figure 5.3 Maximum Daily Mean PM$_{10}$ Concentration, 385 Site Months 1992-1994.



Note: Based on ratified data.

which pollutants have well characterised motor vehicle sources.

5.2.2 Particulate Sulphuric Acid and Ammonium Sulphate

The earliest urban measurements of particulate sulphuric acid were made during the London smog episode in December 1952, when reported concentrations were especially high. Continuous measurements of both particulate sulphuric acid and sulphate aerosol in the United Kingdom were made as part of the Teesside Mist Study in the late 1960's. Although urban concentrations were significantly elevated, on occasions rural concentrations could be elevated as well by the drift of suspended particulate material out of the industrial conurbations.

With the discovery of photochemical ozone formation in the United Kingdom and the associated haze production (Atkins, Cox and Eggleton, 1972), much of the interest in particulate sulphur compounds switched from their health impacts to their role in visibility reduction. Elevated hourly concentrations of particulate sulphuric acid and ammonium sulphate were reported together with ozone concentrations in the range 80-100 ppb, during July 1971, at Harwell, Oxfordshire.

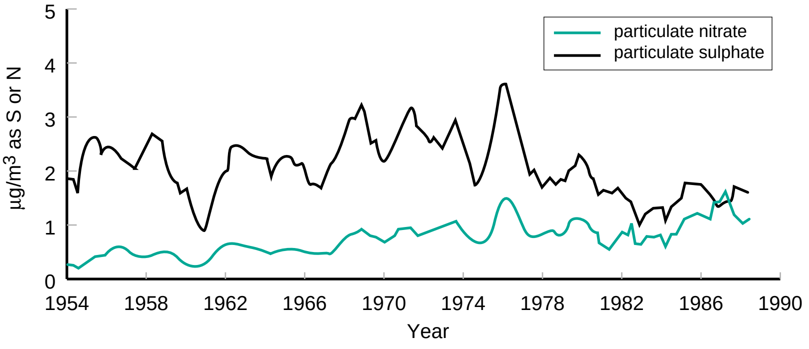
Long term time series of total particulate sulphate concentrations are available from 1954 onwards for Chilton near Harwell in Oxfordshire (Lee and Atkins, 1994) and are shown in Figure 5.4. The concentrations are reported as µg S/m^3 and show a steady rise through the 1950s and 1960s to a maximum in the 1970s, when concentrations started to fall through to the present day. Because of the relatively long lifetime of particulate sulphate, these concentrations are thought to be representative of a rather wide area of southern England.

The rise in particulate sulphate observed at Harwell, Oxfordshire since the 1950s and its subsequent decrease is reflected in the longer term record of sulphur deposition in Greenland ice (Mayewski et al, 1986). Here the growth in use of sulphur-containing fossil fuels can be clearly detected as setting in around the mid-19th century. A more recent decline is also detectable showing that the pattern observed in southern England is likely to have been reproduced throughout much of continental Europe.

The growth in interest in acid rain and environmental acidification in Europe during the 1970s prompted the establishing of the UNECE European Measurement and Evaluation Programme (EMEP) and a monitoring network for particulate sulphate in rural areas across Europe. By the 1990s, a network of over one hundred stations has been established, reporting monthly mean particulate sulphate concentrations (Schaug et al, 1994). Results are presented in Figure 5.5 for the entire EMEP network, showing a clear gradient in levels across the UK from about 1.5 µg S/m^3 in the south and east to about 0.5 µg S/m^3 in the north and west, which approaches a factor of three.

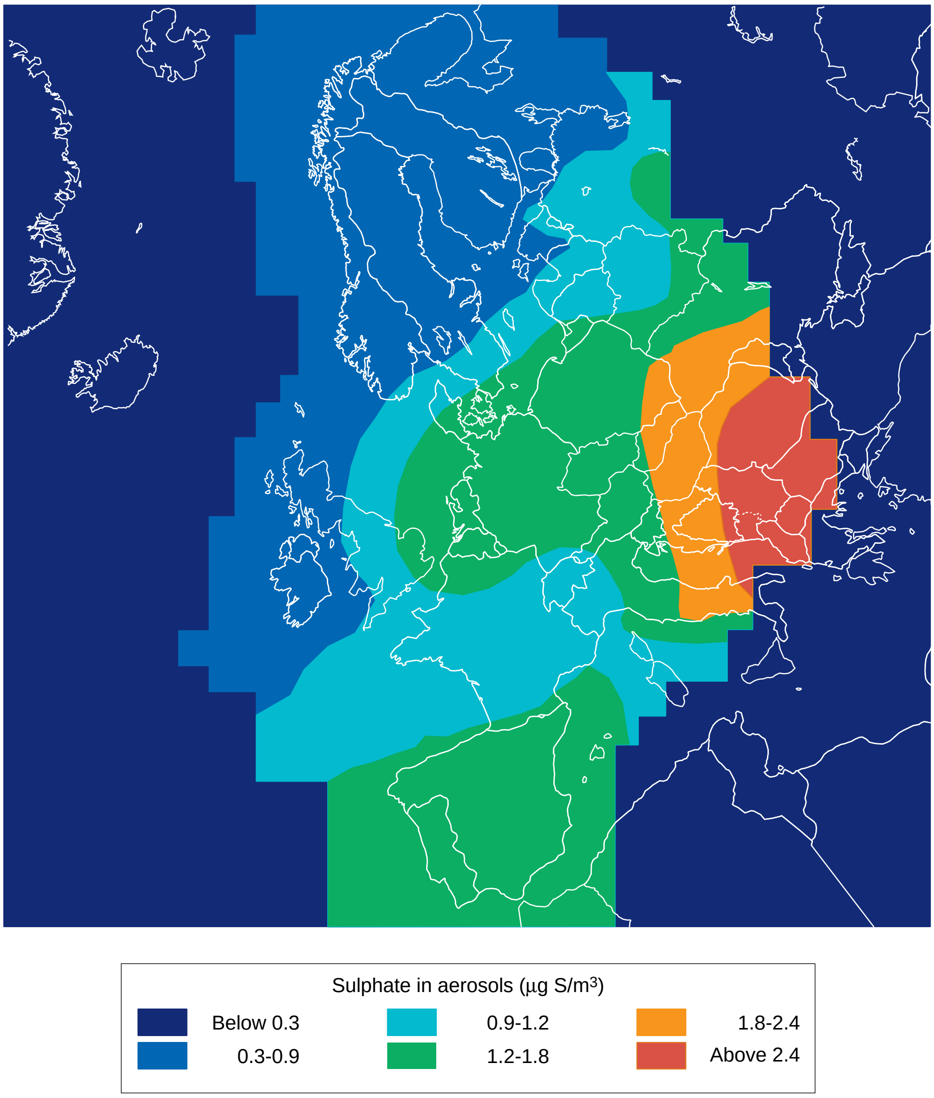
Urban monitoring of particulate sulphate levels started in the UK during the 1970s at a handful of sites and

Figure 5.4 Three-month Running Mean Concentration of Particulate Sulphate and Particulate Nitrate at Chilton, 1954 to 1988.



Source: RGAR, 1990.

Figure 5.5 Sulphate in Aerosols Across Europe, 1993.



Source: Hjellbrekke et al, 1995.

confirmed the importance of photochemical oxidation as the main source, as in the rural areas. Mean UK urban concentrations tended to be similar to rural levels, confirming that long range transport rather than urban scale production was the dominant source of the elevated urban summertime particulate sulphate concentrations.

With the onset of national urban PM$_{10}$ monitoring in the United Kingdom in 1992, increasing interest has been given to assessing the contribution made by particulate sulphuric acid and ammonium sulphate to urban PM$_{10}$ levels. Almost all the rural measurements of particulate sulphur compounds are reported as µg S/m^3 and so are not directly comparable with urban PM$_{10}$ measurements reported as µg/m^3. A simple conversion factor does not exist, but a rather good guide can be obtained if results in µg S/m^3 are scaled by a factor of about 4. Assuming that rural concentrations can be taken as a guide to urban concentrations, baseline urban levels of particulate sulphate of the order of 6 µg/m³ on a PM_{10} basis can be anticipated.

The strongest evidence that photochemically-generated secondary particulate sulphate contributes to urban PM_{10} measurements comes from an analysis of the AUN PM_{10} data itself. Monthly mean PM_{10} concentrations exhibit a significantly different seasonal cycle to that of the typical primary pollutants such as carbon monoxide, NO_x and some of the VOCs. PM_{10} levels tend to be highest in autumn and winter, as do the typical primary pollutants, but differ in that summer mean levels are only slightly lower, whereas they are significantly lower for the primary pollutants. These points are illustrated in Table 5.1 and Figure 5.3 with the available national PM_{10} data for 1992-1994.

PM_{10} levels tend to rise during summertime photochemical episodes and at several sites simultaneously in response to the changing meteorological situation (see Figure 5.6 and Figure 8.4). In this respect, the behaviour shown by urban PM_{10} concentrations is reminiscent of that of rural ozone concentrations. Summertime maximum hourly ozone concentrations appear to correlate well with maximum daily mean PM_{10} concentrations at some AUN sites. Hourly PM_{10} and ozone concentrations tend not to correlate well because ozone shows a characteristic diurnal variation which is not shared by PM_{10}, since it lacks the efficient nocturnal depletion mechanisms of dry deposition and chemical reaction with NO exhibited by ozone.

The highly time-resolved hourly measurements of particulate sulphuric acid and ammonium sulphate concentrations reported during the photochemical episode during 1971 show that it is indeed likely that much or all of the urban PM_{10} currently measured during the summertime could be accounted for by the regional scale transport of photochemically oxidised sulphur compounds. In which case, the majority of the particulate sulphur is anticipated to be present in the accumulation mode, in the particle size range 0.1-0.3 µm. In this size range its dry deposition velocity is at a minimum, and its lifetime many days.

5.2.3 Particulate Ammonium and Other Nitrates

Although particulate nitrate and sulphate share many common features, their formation mechanisms and atmospheric behaviour are in fact rather different. The processes involved with particulate nitrate are only being slowly understood and are complicated by measurement inadequacies, artefacts and lack of coverage.

Nitrate can be detected in suspended particulate material and its presence usually correlates well with that of sulphate showing some measure of association. The long-term time-series of particulate nitrate concentrations measured at Harwell, Oxfordshire (Lee and Atkins, 1994) shows a steady rise throughout the period from 1954 onwards, without the recent decrease observed for particulate sulphate (Figure 5.4). Again, this behaviour parallels that of nitrate in Greenland ice (Mayewski et al, 1986) since preindustrial times.

The UNECE EMEP programme has established a network for total inorganic nitrate, which includes both particulate nitrate and gaseous nitric acid, although fewer sites have contributed on a historic basis compared with those measuring particulate sulphate. Table 5.2 shows the data for the UK monitoring sites. Clearly human activities produce elevated nitrate aerosol concentrations and a gradient is likely to exist in concentrations across the UK as with sulphate aerosol.

No long-term routine measurements of particulate nitrate aerosol appear to have been made in urban areas of the UK. Measurements have been reported for urban and rural areas of Essex by Harrison and Allen (1990). There is no reason to expect that particulate nitrate aerosol is not an ubiquitous contributor to urban PM_{10} levels. Indeed, measurements made in the Los Angeles basin show that particulate nitrate is the major inorganic contributor to urban PM_{10} levels in that city.

The main fate of the NO_x emitted in urban and rural areas is oxidation to nitric acid vapour by hydroxyl radicals during daytime and by ozone to N_2O_5 at night. Sulphuric acid produced by the oxidation of sulphur

TABLE 5.1 Maximum Daily Mean PM$_{10}$ Concentrations for National Network Stes (µg/m^3).

Site	Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec
London Bloomsbury	1992	85	68	51	94	47	75	68	41	66	43	43	79
	1993	66	76	68	75	81	100	54	50	44	48	81	29
	1994	42	75	31	41	57	54	58	41	46	93	58	91
Belfast	1992	-	-	20	30	56	45	28	28	95	136	95	248
	1993	120	61	66	73	78	107	25	42	65	118	98	40
	1994	39	162	38	40	57	49	42	30	66	83	55	191
Edinburgh	1992	-	-	-	-	-	-	-	-	-	32	29	72
	1993	36	38	43	43	41	46	-	37	32	45	66	35
	1994	33	43	25	25	42	38	41	28	25	62	38	49
Newcastle	1992	-	-	37	71	66	72	48	51	67	40	40	71
	1993	42	62	54	65	45	79	63	-	-	38	73	43
	1994	50	63	33	43	52	51	51	37	53	77	58	59
Birmingham Centre	1992	-	-	27	69	77	64	71	60	57	59	34	131
	1993	42	26	56	102	57	79	27	40	66	44	71	27
	1994	33	63	30	30	43	43	46	39	36	71	56	113
Cardiff	1992	-	-	-	-	-	38	36	45	52	48	69	85
	1993	61	52	59	89	65	75	54	-	-	-	62	45
	1994	60	68	59	64	58	81	82	96	80	76	72	43
Leeds	1993	57	62	71	50	42	50	29	52	60	51	96	43
	1994	62	59	33	34	41	46	55	51	60	114	76	77
Bristol	1993	37	63	53	75	57	61	58	44	61	49	81	49
	1994	54	71	34	33	47	42	41	40	40	83	49	52
Liverpool	1993	-	-	-	93	74	-	29	44	85	48	163	49
	1994	51	76	32	29	52	39	47	39	58	84	59	76
Birmingham East	1993	-	-	-	-	-	-	-	-	-	-	-	31
	1994	51	57	26	26	37	41	45	32	33	62	79	106
Southampton	1994	50	39	33	55	39	45	48	35	40	63	53	43
Leicester	1994	59	50	25	30	36	39	42	40	33	51	52	65
Hull	1994	56	73	34	37	58	37	52	46	48	85	62	55
London Bexley	1994	-	-	-	-	27	44	58	33	41	70	58	49
Swansea	1994	-	-	-	-	-	-	-	-	-	-	-	46

Figure 5.6 Daily Maximum PM_{10} May to June 1993.

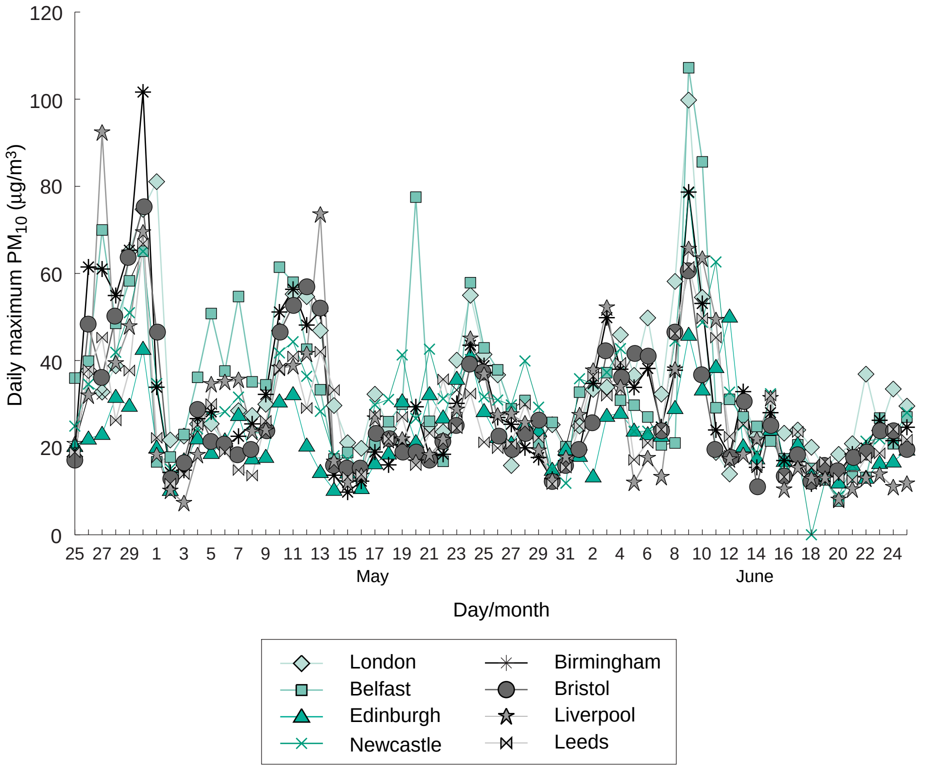


Table 5.2 Nitrate Plus Nitric Acid Data from the EMEP Monitoring Network, 1992 (µg N/m^3).

Site	Annual Mean	Standard Deviation	Minimum	Maximum
Eskdalemuir	0.39	0.63	0.0	4.93
High Muffles	0.88	0.95	0.03	6.51

Source: Schaug et al, 1994.

dioxide can readily self-nucleate to form particulate material or can be adsorbed to pre-existing particles to produce accumulation mode aerosol. Nitric acid vapour does not share this property of self-nucleation. Furthermore, those accumulation mode particles which are loaded up with acidic sulphur compounds are not expected to take up nitric acid vapour efficiently. Nitric acid can however be adsorbed by sea-salt particles displacing HCl, leaving sodium nitrate aerosol. Alternatively, it may react with gaseous ammonia to form ammonium nitrate which may itself be adsorbed by accumulation mode particles. During nightime, N_2O_5 itself reacts with sea salt particles to produce sodium nitrate aerosol. So there are mechanisms by which particulate nitrate can be formed; however, they are likely to have a markedly variable efficiency compared with those for particulate sulphate.

The evidence that particulate nitrate is associated with summertime photochemical episodes is more difficult to find. Nevertheless, it is likely that regional scale photochemical production of particulate nitrate does occur and that this contributes to urban PM_{10} concentrations in the UK. Almost all the rural measurements of particulate nitrate are reported as µg N/m^3 and so are not directly comparable with urban PM_{10} measurements reported as µg/m^3. A simple conversion factor does not exist, but a rather good guide can be obtained if results in µg N/m^3 are scaled by a factor of about 4. Assuming that rural concentrations can be taken as a guide to urban concentrations, baseline urban levels of particulate nitrate of the order of 4 µg/m³ on a PM_{10} basis can be anticipated. This secondary contribution to urban PM_{10} is somewhat smaller than that of particulate sulphate but is still quite significant.

5.2.4 Impact of Present Policies On Future Secondary PM_{10} Air Quality

The spatial distribution of the secondary aerosol concentrations has been calculated with the Hull Acid Rain Model (HARM) at a spatial resolution of 20kmx20km across the United Kingdom. The model treats both European and UK sources of sulphur dioxide, nitrogen oxides, ammonia and hydrogen chloride, together with their interacting chemistry, dry deposition and wet removal. The spatial patterns calculated of the particulate concentrations of sulphate, nitrate, chloride and ammonium agree with the available observations, such as they are. Figure 5.7 illustrates the geographical variation in the model-calculated concentrations, with a peak in the south east and a minimum in the north west of Britain. The model aims to give a detailed source attribution of the secondary PM_{10} aerosol species across the United Kingdom. Full details of the model are given elsewhere (Metcalfe et al 1995).

It has been possible to estimate how the distribution of secondary PM_{10} will respond to policy measures already in hand by developing an emission scenario for the year 2010. This scenario has then been used in the HARM model to estimate future secondary PM_{10} contributions. The elements of the emission scenario are as follows:

- the Oslo Protocol to the UNECE international convention on Long Range Transboundary Air Pollution, which should lead to about a 60% reduction in sulphur dioxide emissions across Europe by the year 2010 on present day levels,

- the Sofia Protocol to the UNECE international convention which should lead to a freeze on nitrogen oxide emissions at 1987 levels,

- the installation of three-way catalyst technologies on petrol-engined motor vehicles in the EU countries and Norway and some limited action on diesel vehicle emissions during the late 1990s in line with the proposals of the European Commission,

- NO_x emissions from Large Combustion Plant in the UK have been assumed to decrease in accord with the EC Directive and stay constant from 1997 onwards,

- HCl emissions are assumed to decrease in line with power station SO_2 emissions,

- no action has been assumed on ammonia emissions across Europe.

Mean PM_{10} contributions across Great Britain are tabulated in Table 5.3 in both scenarios. There appears to be a 39% reduction in secondary PM_{10} to be anticipated by the year 2010 due to present policies. The result will be a future secondary aerosol which is largely composed of nitrate.

5.2.5 Semi-Volatile Organic Compounds

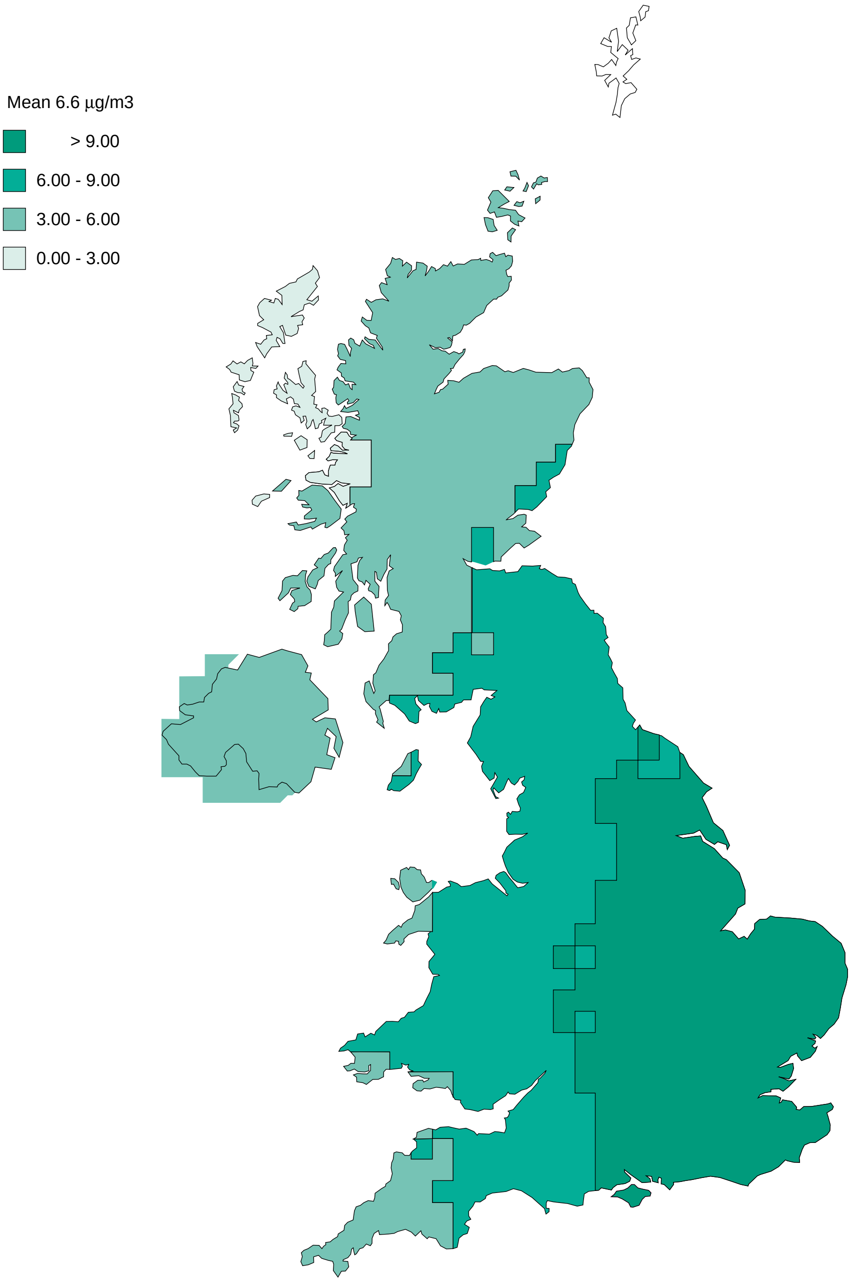
It has been long recognised that large quantities of organic compounds are emitted into the urban atmosphere. The main sources involve evaporation or fuel spillage, natural gas leakage, solvent usage, industrial and chemical processes and the use of bitumen and road asphalt. The sources of much of the

Table 5.3 Contribution from the Major Aerosol Species to PM_{10} in the Present Day and Future Atmospheres as Calculated in the HARM Model.

Contribution	**Present Day PM_{10}, µg/m³**	**Future 2010 PM_{10}, µg/m³**
Sulphate	2.8	1.2
Nitrate	2.9	2.2
Ammonium	0.7	0.5
Chloride	0.1	0.1
Total	6.5	4.0

Source: Metcalfe et al, 1995

Figure 5.7 Secondary PM_{10} Concentration as Calculated by the HARM Model.



Source: Metcalfe et al, 1995.

low-molecular weight organic compounds have been quantified for the UK. This material is of high volatility generally and is readily removed from the atmosphere over a period of days to years by atmospheric oxidation. However, as molecular weight increases, volatility decreases and there comes a point when the atmospheric behaviour of the more complex organic compounds changes radically from that exhibited by the low-molecular weight compounds.

For some organic compounds volatility is so low that evaporation is an exceedingly slow process. Emissions to the atmosphere occur through some form of high temperature process such as firing, curing or melting as with the laying of road asphalt. Under these circumstances, the emitted organic compounds rapidly cool and condense on any pre-existing particles in the atmosphere. Although nucleation mode particles are the most numerous in urban areas, they do not offer the large superficial area as that provided by the

Table 5.4 Concentrations of Organic Compounds Formed in Air Samples Taken in Belgium, (reprinted courtesy of Elsevier Science Ltd).

Compound	Concentration (ng/m³) Particle Samples P	 Gas-phase Samples G	 Distribution Factor P/G
Aliphatic Hydrocarbons			
n-nonadecane	0.80	15.1	0.053
n-eicosane	0.85	7.55	0.113
n-heneicosane	1.08	4.12	0.262
n-docosane	2.33	4.23	0.551
n-triosane	4.75	3.38	1.41
n-tetracosane	8.15	4.63	1.76
n-pentacosane	9.50	5.74	1.66
n-hexacosane	9.73	8.70	1.12
n-heptacosane	11.1	9.03	1.39
n-octasane	8.10	7.80	1.04
n-nonacosane	15.8	7.32	2.41
n-tricontane	5.75	4.87	1.18
n-hentriacontane	11.2	3.99	2.81
Polyaromatic Hydrocarbons			
Phenanthrene and anthracene	1.21	44.7	0.027
Methylphenanthrene and methylanthracene	0.90	10.2	0.088
Fluoranthene	2.22	8.52	0.261
Pyrene	3.17	3.36	0.488
Benzofluorenes	2.33	1.87	1.246
Methylpyrene	0.93	-	P
Benz(a)anthracene and chrysene	12.2	3.87	3.15
Benzo(k)fluoranthene and benzo(b)fluoranthene	23.1	2.01	11.5
Benzo(a)pyrene, benzo(e)pyrene and perylene	20.1	2.69	7.47
Phthalic Acid Esters			
di-isobutylphthalate	1.73	32.8	0.053
di-n-butylphthalate	101	353	0.286
di-2-ethylhexylphthalate	54.1	127	0.426
Miscellaneous			
Anthraquinone	1.59	5.66	0.281
Fatty Acid Esters			
Lauric acid	0.01	30.3	0.0003
Myristic acid	1.39	7.58	0.183
Pentadecanoic acid	3.60	5.35	0.673
Palmitic acid	29.0	4.77	6.08
Heptadecanoic acid	2.84	5.71	0.497
Oleic acid	2.06	-	P
Stearic acid	35.7	2.27	15.73
Nonadecanoic acid	1.91	1.02	1.87
Eicosanoic acid	9.04	3.00	3.01
Heneicosanoic acid	2.56	1.65	1.55
Docosanoic acid	13.7	-	P
Tricosanoic acid	3.23	-	P
Tetracosanoic acid	10.7	-	P

Table 5.4 Concentrations of Organic Compounds Formed in Air Samples Taken in Belgium, (reprinted courtesy of Elsevier Science Ltd)(cont.).

Compound	Concentration (ng/m^3) Particle Samples P	Gas-phase Samples G	Distribution Factor P/G
Pentacosanoic acid	2.55	-	P
Hexacosanoic acid	9.12	-	P
Aromatic acids			
Pentachlorophenol	2.43	-	P
Basic Compounds			
Acridine, phenanthridine and benzoquinolines	0.94	-	P
Benzacridines	0.85	-	P

Source: Cautreels and Van Cauwenberghe (1978)

Low molecular-weight organics found only in the gas phase were not included in this extract of the authors' original table.

P in the last column indicates that essentially all of the material was in particle form.

accumulation mode particles. So the high-molecular weight organic compounds tend to attach themselves rapidly in timescales of seconds to minutes to the accumulation mode particles and hence contribute to urban PM_{10} levels.

Table 5.4 illustrates how with increasing molecular weight and decreasing volatility, organic compounds become increasingly attached to particles rather than remain in the gaseous phase. This data is taken from Cautreels and Van Cauwenberghe (1978) and refers to measurements made in urban areas of Belgium. The table confirms that a wide range of aliphatic hydrocarbons, polyaromatic hydrocarbons, oxygenates, aromatic acids, esters and nitrogen-containing organic compounds are taken up by the accumulation mode aerosol and contribute to the secondary particulate material present in urban areas.

5.3 KEY POINTS

- *Secondary particles are formed in the atmosphere, mostly from the oxidation of sulphur and nitrogen oxides.*
- *The main components of secondary particulate matter are ammonium nitrate and ammonium sulphate from ammonia neutralisation of sulphuric and nitric acids, and semi-volatile organic matter.*
- *Airborne concentrations of sulphate measured in southern England have decreased in recent years, whilst concentrations of nitrate have increased steadily since measurements began in 1954.*
- *Numerical modelling of the impact of currently agreed controls on emissions of sulphur and nitrogen oxides predicts a reduction in secondary PM_{10} concentrations across the UK of 39% by the year 2010. Nitrate will be the dominant component at that time.*
- *A wide range of semi-volatile organic compounds can condense on atmospheric particles. Few measurements of this component are available in the UK.*

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6 Concentrations and Trends in Particulate Matter

6.1 INTRODUCTION

Particulate matter, unlike other ambient atmospheric pollutants, tends to be classified by the measurement technique used. Thus, PM_{10}, $PM_{2.5}$, black smoke, strong acid aerosol, total suspended particulate are all terms which are used to characterize the physical or chemical state of airborne particulate matter and which give an indication of the measurement method employed.

Historically, filter methods were first employed to measure the concentrations of particulate matter. The material collected on a filter paper for a specified interval, typically a day, was analysed by weighing or by determining the intensity of the black stain produced (the “black smoke” or “smoke stain” method). Measurements have been made at certain sites which go back to the early part of this century. Although these sampling methods continue to be used and do provide extensive spatial and temporal coverage, automatic analysers such as the tapered element oscillating microbalance (TEOM) have recently been introduced in the United Kingdom and are increasingly being used to give measurements on a finer timescale. There has been a tremendous increase in the amount of data available in the United Kingdom on particulate matter as PM_{10} since the introduction of these instruments and the emphasis of this Chapter will be primarily on these newer measurements.

The general picture gained from the measurements, especially from the smoke and sulphur dioxide networks, is of a dramatic decline in the levels of particulate matter over the course of the last 40 years. The introduction of smoke control areas after the London smog episodes of 1952 and 1962, the shift away from coal burning for space heating and cooking in most parts of the UK (Northern Ireland excepted) and the "tall stack" policy have greatly reduced the emissions of particulate matter and their ambient concentrations.

Although the levels of particulate matter are now significantly lower than those observed historically, the epidemiological studies undertaken recently, most notably in the United States (Dockery et al, 1993; Pope et al, 1995), have once again focussed attention on current levels of particulate matter. This Chapter will review the measurements made by the different monitoring techniques in both urban and rural environments, will seek to identify trends in the concentration of particulate matter, to discern relationships with other pollutants and ultimately to see whether the sources of particulate matter can be identified.

6.2 MEASUREMENTS OF PARTICULATE MATTER

The different measurement techniques used to characterize particulate matter were described in Chapter 3 of this report. At the present time, measurements of particulate matter are made on a routine basis in three national networks:

(1) the Basic Urban Network for smoke and sulphur dioxide, in which daily concentrations of particulate matter are determined using the “smoke stain” method. The measurements made in this network represent the longest running series of data. Sites were chosen to be representative of locations in major population centres whilst ensuring spatial coverage of the whole country. The network currently comprises 154 sites, 84 of which are also included in the EC Directive network described in (2) below.

(2) the EC Directive network for smoke and sulphur dioxide, in which daily concentrations of particulate matter are again determined using the smoke stain method. This network was established to monitor compliance with the EC Directive (80/779/EC) on Sulphur Dioxide and Suspended Particulate Matter. It currently comprises 155 sites. The measurements are specifically made at sites which were at risk of breaching the Directive or where breaches have occured. The number of sites has fallen from a peak of 330 sites in 1986 as levels of smoke have declined (QUARG, 1993a).

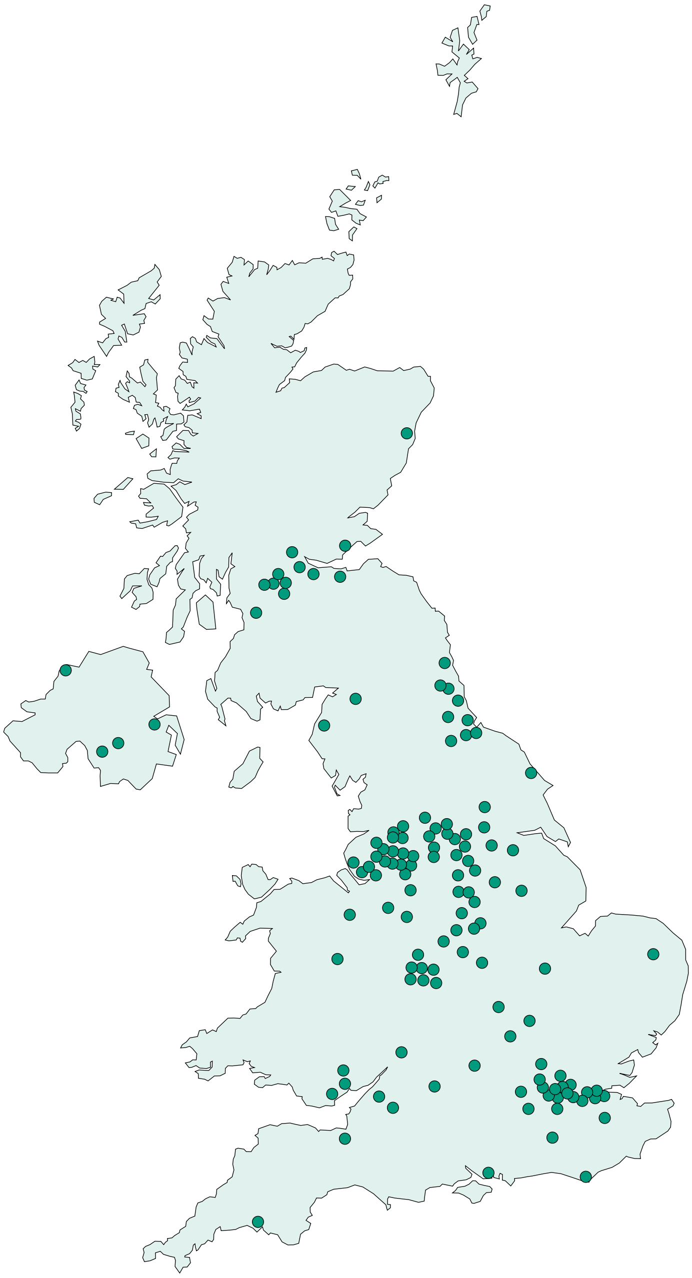
(3) the Automatic Urban Network, in which hourly concentrations of particulate matter are determined as PM_{10} using tapered element oscillating microbalance (TEOM) instruments. The network was established in 1992 and now comprises 16 sites positioned in urban background locations.

- Belfast
- Bristol
- Birmingham (Centre)
- Birmingham (East)
- Cardiff
- Edinburgh
- Kingston-upon-Hull
- Leeds
- Leicester
- Liverpool
- London (Bexley)
- London (Bloomsbury)
- Middlesbrough
- Newcastle
- Southampton
- Swansea

The network is set to expand, with the establishment of a further 13 sites by the end of 1996.

In addition the Department of the Environment has announced that it intends to integrate around 35 locally operated sites into the national network by 1996. Some of these sites are expected to monitor PM_{10}.

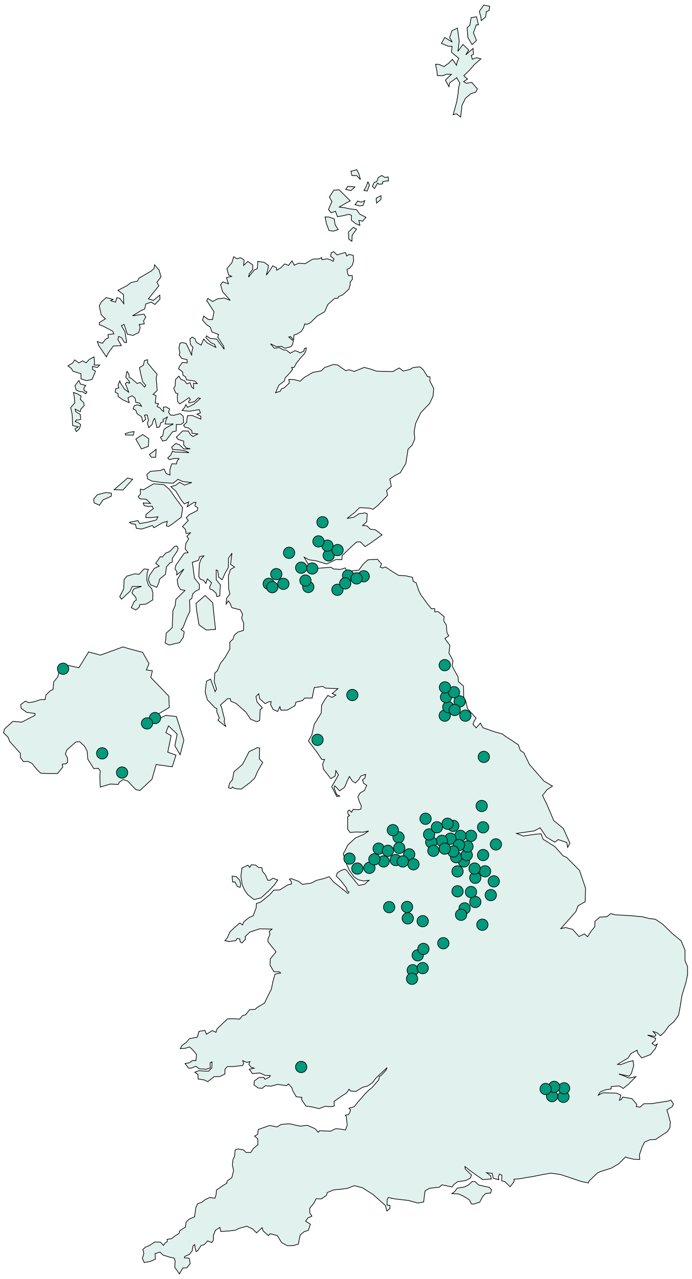
Figure 6.1 Basic Urban Network Sites, 1993/94.



Figures 6.1 to 6.3 present the positions of the current monitoring sites in these networks across the United Kingdom.

The Basic Urban and EC Directive networks grew out of the National Survey for smoke and sulphur dioxide which was started in 1961. The objective of the National Survey was to monitor the implementation of smoke control measures. Although many of the original sites are still operational, the number of sites has fallen from a peak of 1410 in 1967/68. The measurements made in this network represent the longest running series of data and, in the absence of historical PM_{10} measurements, have been widely used in epidemiological studies. (The relationship between black smoke and PM_{10} is discussed in section 6.4.2).

Figure 6.2 EC Directive Network Sites, 1993/94.

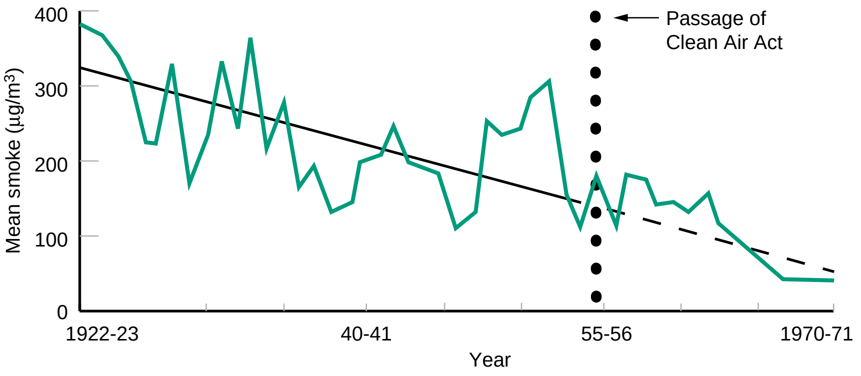


Following the reorganisation of the National Survey network in 1981 into the Basic Urban and EC Directive networks, the sites in non-urban environments were subsequently transferred to the UK Acid Deposition network. Measurements of smoke have not been undertaken at rural sites since 1991.

In addition, there are long-term time-series measurements of particulate sulphate and nitrate which have been made at Chilton, Oxfordshire and of particulate sulphate at 8 rural sites. In the "multi-element" survey, which was started in 1976, a range of trace elements, including lead, are currently measured at 5 urban sites. Previously, a series of measurements of strong acid aerosol had been made by the Medical Research Council's Air Pollution Unit based at St Bartholomew's Hospital between 1963 and 1972. Other measurements of particulate matter

Figure 6.3 DoE PM_{10} Particulate Matter Air Quality Network, Operational Sites (as at September 1995).

Figure 6.4 **Average Smoke Levels at Kew during October-March 1922-3 to 1970-71.**



Source: Clout, 1978.

have been made over shorter periods at several locations around the country.

With the increased concern about particulate matter, a number of local authorities in the United Kingdom have recently established monitoring sites to measure PM_{10}. Some of these sites are situated in roadside locations and are beginning to provide extremely valuable data on concentrations of particulate matter in these locations which complement the more extensive sets of measurements made in urban background locations.

6.3 MEASUREMENTS AND TRENDS IN PARTICULATE MATTER

6.3.1 Black Smoke Measurements

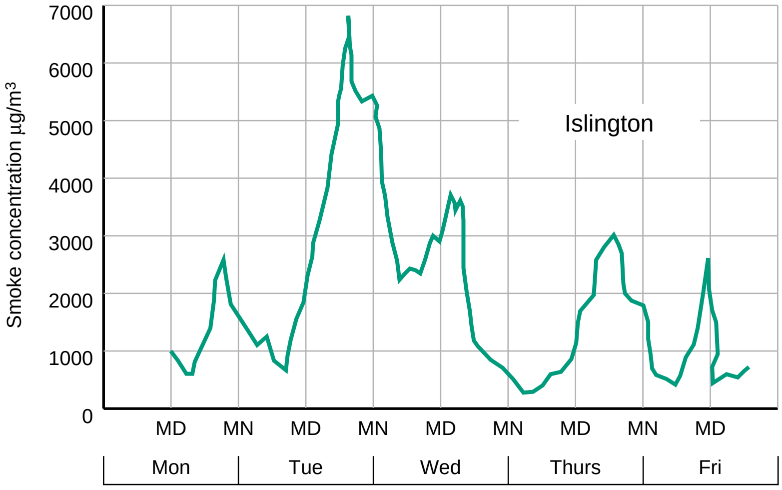
Historically, particulate matter has been measured using filter sampling techniques and extensive datasets exist for specific sites back to the early part of this century. Figure 6.4 shows the mean concentrations of smoke measured between October and March at the Kew Observatory between 1922/23 and 1970/71 using the smoke stain method (Clout, 1978). The figure shows a tenfold decline in the mean levels of smoke over this period.

In December 1952 and again in December 1962, two major “smog episodes” occurred in London. Hourly measurements of smoke made at three London sites in the 1962 episode are shown in Figure 6.5 (MAAPE, 1992). The highest recorded hourly level was observed at the Islington site and was in excess of 6000 µg/m³. Although the levels of sulphur dioxide recorded in the 1962 episode were comparable to those observed in the earlier episode, the overall concentrations of smoke were much lower. Indeed, during the 1952 episode, many of the samplers were overloaded. Epidemiological studies of the 1952 and 1962 smog episodes indicated that 4000 and 700 excess deaths respectively could be associated with the elevated pollution levels present during the episodes (see also Chapter 9).

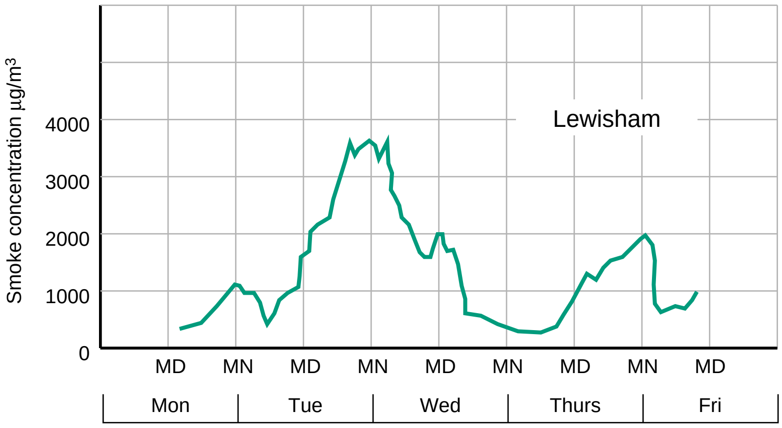
Following these major smog episodes in London, Clean Air Acts were introduced in 1956 and 1968. Although these Acts had an effect on the concentrations of smoke observed in urban environments through the creation of smoke control areas, other features such as the long-term shift away from siting power stations in urban environments, the use of fuels other than coal for space heating and domestic cooking and the construction of taller stacks were as significant in reducing the concentration of smoke. Figure 6.6 illustrates the decline in smoke concentrations observed at specific sites located in Belfast, London (Lambeth), Stoke-on-Trent and Norwich. Smoke concentrations fell rapidly during the 1960s and 1970s but there has been a slower decrease in smoke levels through the 1980s and 1990s which may, in part, reflect the increasing emissions of smoke from road traffic.

Coal burning areas in the UK still show some of the highest concentrations although, as elsewhere, these

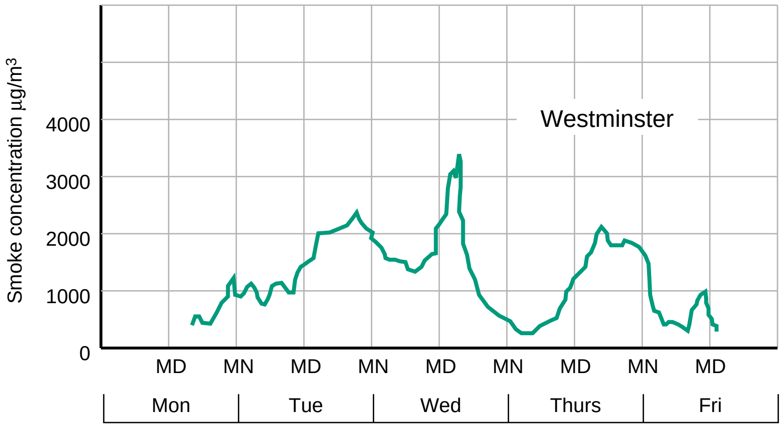
Figure 6.5 Hourly Smoke Concentrations in 1962 Smog Episode.



London fog, 1962. Hourly smoke concentrations at Islington, 3rd-7th December.



London fog, 1962. Hourly smoke concentrations at Lewisham, 3rd-7th December.



London fog, 1962. Hourly smoke concentrations at Westminster, 3rd-7th December.

Source: MAAPE, 1992.

Figure 6.6 Trend in Annual Arithmetic Mean Concentrations of Smoke at Selected Sites.

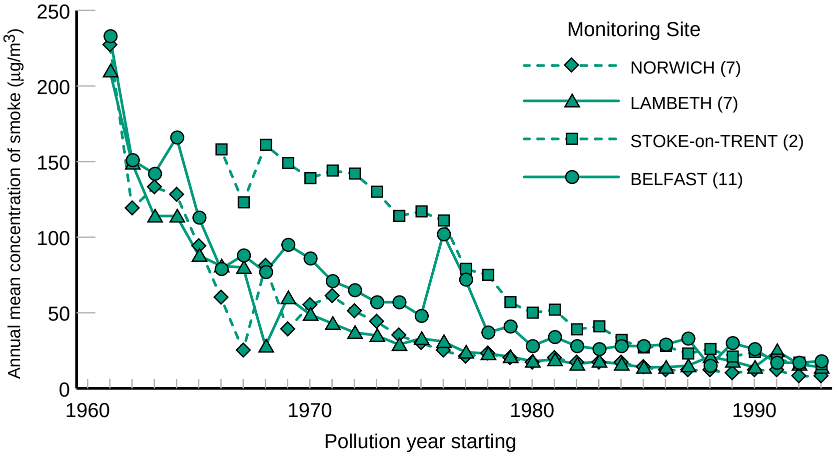
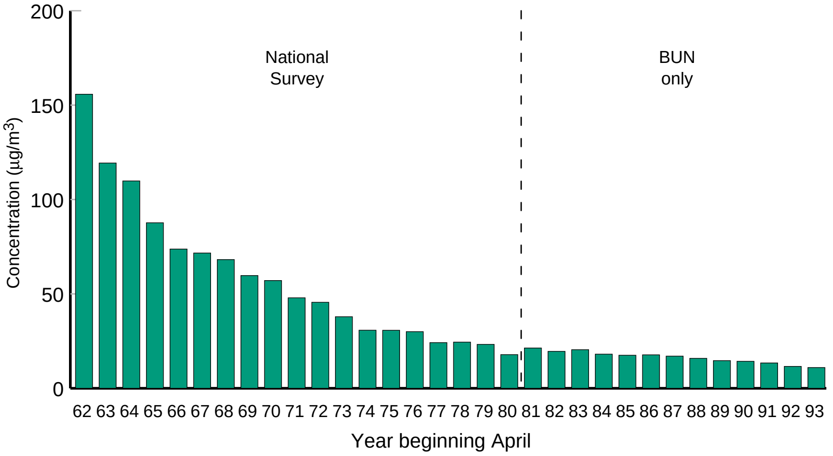


Figure 6.7 Annual Mean Black Smoke Concentration 1962-1993 across the Basic Urban Network.



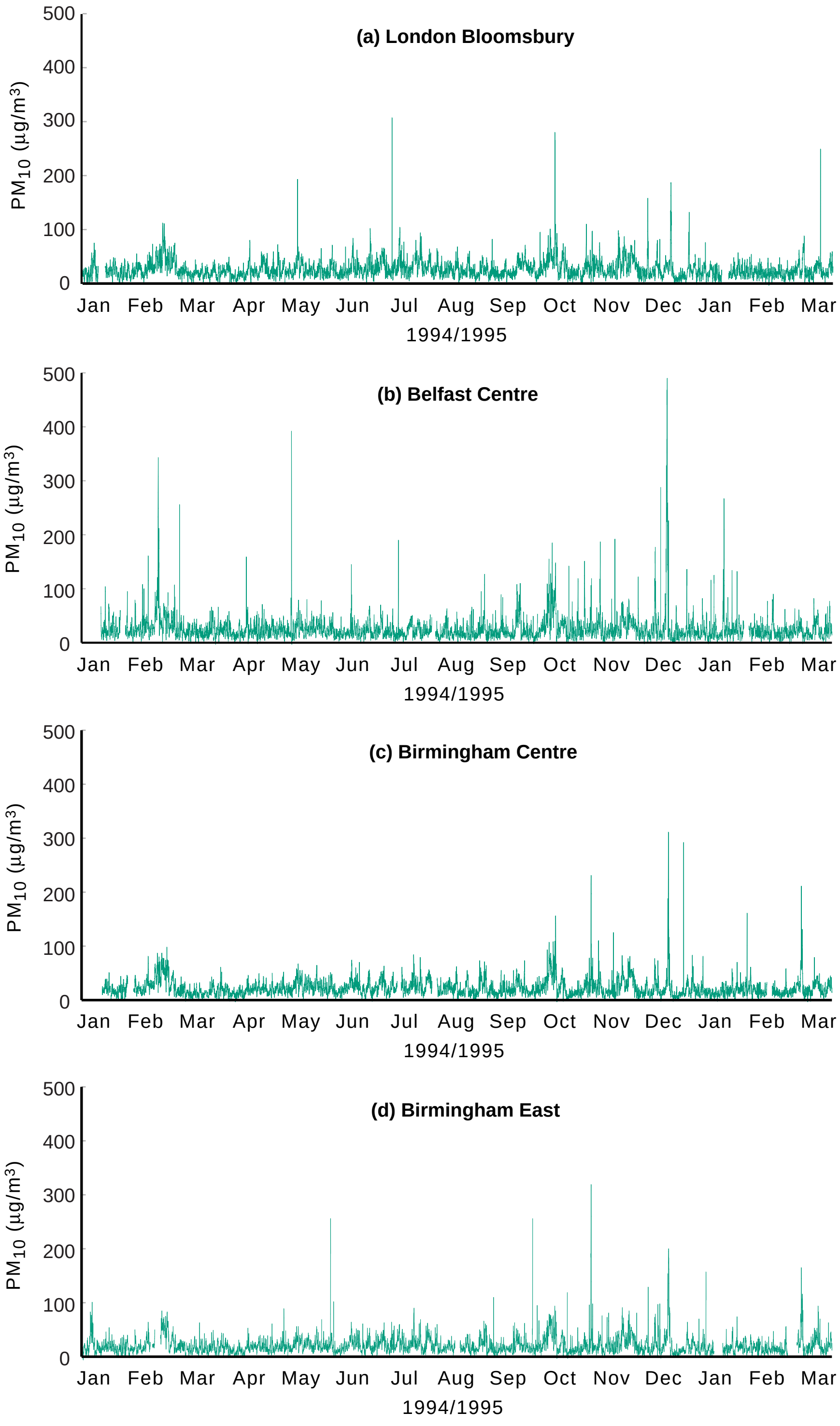
levels have also fallen over the past 30 years. This is illustrated in Figure 6.6 for the site at Belfast. It is interesting to note that the annual mean concentration determined in Belfast is comparable to those observed at London (Lambeth), Stoke-on-Trent and Norwich despite the significantly higher amount of coal burning in Belfast.

Average urban smoke concentrations across the United Kingdom for the pollution year 1962/63 were over 150 µg/m³ (Stevenson et al, 1995). The average concentration of the measurements made in the Basic Urban Network for the pollution year 1993/94 was 11 µg/m³ (Stevenson et al, 1995). The decline in annual mean black smoke concentration over this period can be seen in Figure 6.7. It should be noted that the measurement of smoke has traditionally been made at those sites which were likely to experience elevated levels of smoke as a result of coal burning and therefore these measurements may not necessarily detect enhanced concentrations resulting from motor vehicle emissions.

6.3.2 PM_{10} Measurements

Hourly concentrations of PM_{10} measured at the London Bloomsbury, Belfast, Birmingham and Birmingham East sites for the period from January 1994 to March 1995 are shown in Figures 6.8a to 6.8d. It is clear that on a daily basis or even at the hourly level, there are periods when elevated concentrations of PM_{10} occur simultaneously at a

Figure 6.8 PM$_{10}$ Time Series Plot, Hourly Averages, January 1994 - March 1995.



Note: 1994 data are ratified, 1995 data are provisional.

number of sites (eg PM$_{10}$ measurements in December at Birmingham and London). This observation is demonstrated graphically in Figure 6.9 which presents the daily average levels of PM$_{10}$ recorded at 9 urban sites across the UK between April and June 1993.

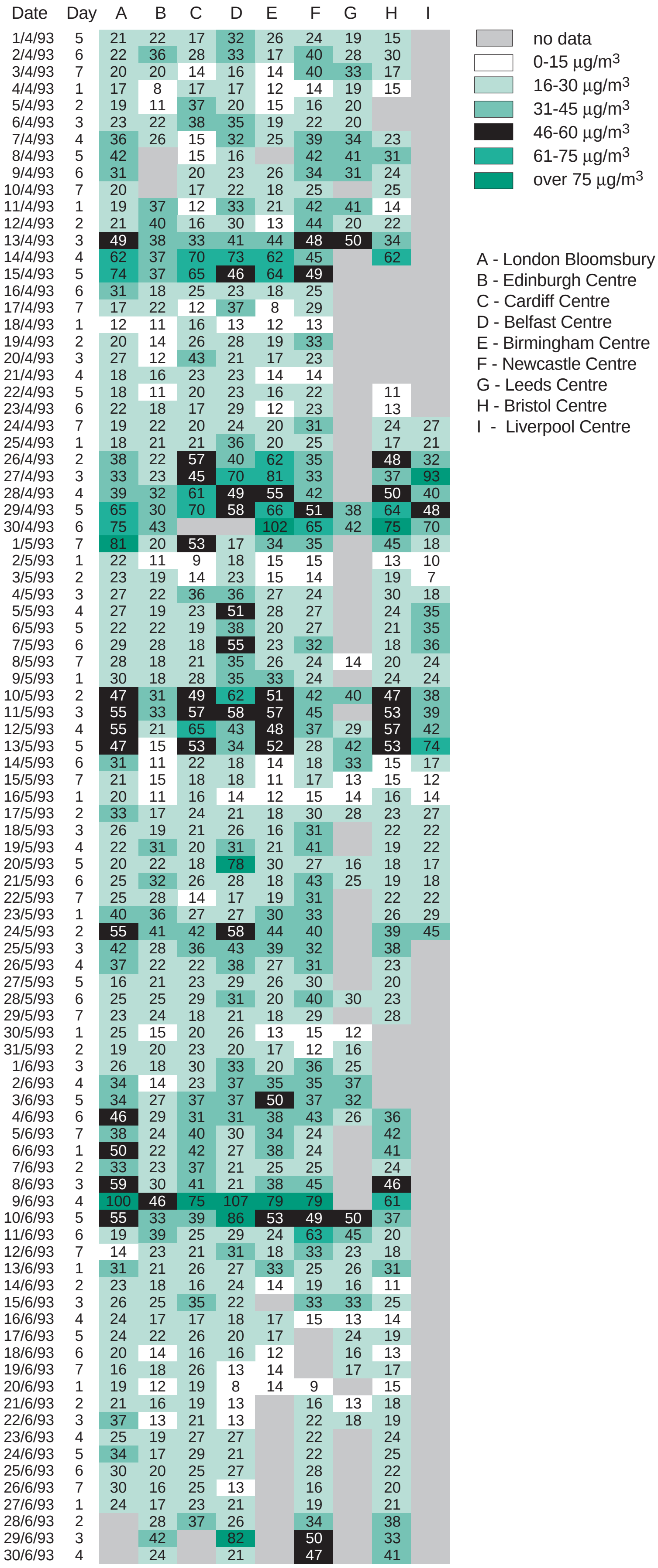
There are also episodes arising from local sources and/or local meteorological conditions. This is particularly the case at the Belfast site where coal burning, in the absence of natural gas, is the main energy source for domestic heating and cooking; in

Table 6.1 - Summary Statistics for Hourly Average PM_{10} for 1993 and 1994 (Bower et al, 1995 and 1996).

	1993 (ratified data)				1994 (ratified data)			
Site	**Annual Mean (µg/m³)**	**98th Percent (µg/m³)**	**Max. Hour (µg/m³)**	**Peak/Mean**	**Annual Mean (µg/m³)**	**98th Percent (µg/m³)**	**Max. Hour (µg/m³)**	**Peak/Mean**
Belfast	32	79	445	13.9	26	66	490	18.8
Bristol	27	64	270	10.0	24	59	612	25.5
Birmingham (Central)	26	66	186	7.2	23	55	311	13.5
Birmingham (East)					21	50	319	15.2
Cardiff					34	76	564	16.6
Edinburgh	23	43	140	6.1	20	41	307	15.4
Hull					26	56	264	10.2
Leeds	27	64	162	6.0	26	64	310	11.9
Leicester					21	50	203	9.7
Liverpool					25	68	257	10.3
London (Bloomsbury)	29	75	140	4.8	27	56	307	11.4
Newcastle					26	60	297	11.4
Southampton					23	48	291	12.7

Notes:
(1) Entries are only given for those sites which were operational for more than 9 months in a given year. The sites at London (Bexley), Swansea and Middlesbrough have not been included for this reason.
(2) 98th percentile values refer to the 98th percentile of daily means.

Figure 6.9 Daily Average PM_{10} Data, April - June 1993 at Nine Urban Sites.



Date	Day	A	B	C	D	E	F	G	H	I
1/4/93	5	21	22	17	32	26	24	19	15	
2/4/93	6	22	36	28	33	17	40	28	30	
3/4/93	7	20	20	14	16	14	40	33	17	
4/4/93	1	17	8	17	17	12	14	19	15	
5/4/93	2	19	11	37	20	15	16	20		
6/4/93	3	23	22	38	35	19	22	20		
7/4/93	4	36	26	15	32	25	39	34	23	
8/4/93	5	42		15	16		42	41	31	
9/4/93	6	31		20	23	26	34	31	24	
10/4/93	7	20		17	22	18	25		25	
11/4/93	1	19	37	12	33	21	42	41	14	
12/4/93	2	21	40	16	30	13	44	20	22	
13/4/93	3	49	38	33	41	44	48	50	34	
14/4/93	4	62	37	70	73	62	45		62	
15/4/93	5	74	37	65	46	64	49			
16/4/93	6	31	18	25	23	18	25			
17/4/93	7	17	22	12	37	8	29			
18/4/93	1	12	11	16	13	12	13			
19/4/93	2	20	14	26	28	19	33			
20/4/93	3	27	12	43	21	17	23			
21/4/93	4	18	16	23	23	14	14			
22/4/93	5	18	11	20	23	16	22		11	
23/4/93	6	22	18	17	29	12	23		13	
24/4/93	7	19	22	20	24	20	31		24	27
25/4/93	1	18	21	21	36	20	25		17	21
26/4/93	2	38	22	57	40	62	35		48	32
27/4/93	3	33	23	45	70	81	33		37	93
28/4/93	4	39	32	61	49	55	42		50	40
29/4/93	5	65	30	70	58	66	51	38	64	48
30/4/93	6	75	43			102	65	42	75	70
1/5/93	7	81	20	53	17	34	35		45	18
2/5/93	1	22	11	9	18	15	15		13	10
3/5/93	2	23	19	14	23	15	14		19	7
4/5/93	3	27	22	36	36	27	24		30	18
5/5/93	4	27	19	23	51	28	27		24	35
6/5/93	5	22	22	19	38	20	27		21	35
7/5/93	6	29	28	18	55	23	32		18	36
8/5/93	7	28	18	21	35	26	24	14	20	24
9/5/93	1	30	18	28	35	33	24		24	24
10/5/93	2	47	31	49	62	51	42	40	47	38
11/5/93	3	55	33	57	58	57	45		53	39
12/5/93	4	55	21	65	43	48	37	29	57	42
13/5/93	5	47	15	53	34	52	28	42	53	74
14/5/93	6	31	11	22	18	14	18	33	15	17
15/5/93	7	21	15	18	18	11	17	13	15	12
16/5/93	1	20	11	16	14	12	15	14	16	14
17/5/93	2	33	17	24	21	18	30	28	23	27
18/5/93	3	26	19	21	26	16	31		22	22
19/5/93	4	22	31	20	31	21	41		19	22
20/5/93	5	20	22	18	78	30	27	16	18	17
21/5/93	6	25	32	26	28	18	43	25	19	18
22/5/93	7	25	28	14	17	19	31		22	22
23/5/93	1	40	36	27	27	30	33		26	29
24/5/93	2	55	41	42	58	44	40		39	45
25/5/93	3	42	28	36	43	39	32		38	
26/5/93	4	37	22	22	38	27	31		23	
27/5/93	5	16	21	23	29	26	30		20	
28/5/93	6	25	25	29	31	20	40	30	23	
29/5/93	7	23	24	18	21	18	29		28	
30/5/93	1	25	15	20	26	13	15	12		
31/5/93	2	19	20	23	20	17	12	16		
1/6/93	3	26	18	30	33	20	36	25		
2/6/93	4	34	14	23	37	35	35	37		
3/6/93	5	34	27	37	37	50	37	32		
4/6/93	6	46	29	31	31	38	43	26	36	
5/6/93	7	38	24	40	30	34	24		42	
6/6/93	1	50	22	42	27	38	24		41	
7/6/93	2	33	23	37	21	25	25		24	
8/6/93	3	59	30	41	21	38	45		46	
9/6/93	4	100	46	75	107	79	79		61	
10/6/93	5	55	33	39	86	53	49	50	37	
11/6/93	6	19	39	25	29	24	63	45	20	
12/6/93	7	14	23	21	31	18	33	23	18	
13/6/93	1	31	21	26	27	33	25	26	31	
14/6/93	2	23	18	16	24	14	19	16	11	
15/6/93	3	26	25	35	22		33	33	25	
16/6/93	4	24	17	17	18	17	15	13	14	
17/6/93	5	24	22	26	20	17		24	19	
18/6/93	6	20	14	16	16	12		16	13	
19/6/93	7	16	18	26	13	14		17	17	
20/6/93	1	19	12	19	8	14	9		15	
21/6/93	2	21	16	19	13		16	13	18	
22/6/93	3	37	13	21	13		22	18	19	
23/6/93	4	25	19	27	27		22		24	
24/6/93	5	34	17	29	21		22		25	
25/6/93	6	30	20	25	27		28		22	
26/6/93	7	30	16	25	13		16		20	
27/6/93	1	24	17	23	21		19		21	
28/6/93	2		28	37	26		34		38	
29/6/93	3		42		82		50		33	
30/6/93	4		24		21		47		41	

▨ no data
□ 0-15 $\mu g/m^3$
▤ 16-30 $\mu g/m^3$
▦ 31-45 $\mu g/m^3$
■ 46-60 $\mu g/m^3$
▩ 61-75 $\mu g/m^3$
█ over 75 $\mu g/m^3$

A - London Bloomsbury
B - Edinburgh Centre
C - Cardiff Centre
D - Belfast Centre
E - Birmingham Centre
F - Newcastle Centre
G - Leeds Centre
H - Bristol Centre
I - Liverpool Centre

Note: Day 1 = Sunday

Table 6.2. An Analysis of the Correlations between Hourly PM_{10} Levels Measured at the AUN site in Edinburgh and the Weather Data for Edinburgh Airport for all Months in 1994.

Month	**Linear Regression Slopes**			
	Windspeed (knots)	**Temperature (Degrees C)**	**Rain during the last hour, 0.1 mm**	**Sunshine Intensity (W/m^2)**
January	-0.403*	-0.789*	-0.099	0.0054
February	-0.406	-0.411	-0.114	0.0174
March	0.010	0.346	-0.289*	0.0169*
April	-0.011	0.256	0.036	0.0111*
May	0.566*	0.954*	0.222	0.0070
June	0.281	0.931*	0.110	0.0200*
July	-0.517	1.005*	0.221**	0.0078
August	0.160	0.852*	0.201	0.0168*
September	-0.278	0.588	-0.054	0.0050
October	-0.724*	0.810	-0.111	0.0035
November	-0.432	-0.555	-0.329*	0.0013
December	-0.942**	-0.766*	-0.104	0.0027

Notes:
* indicates a regression correlation coefficient, $R > 0.2$, $n<744$.
** indicates $R>0.4$, $n<744$.
Based on provisional data

Cardiff, where the monitoring site was affected by building development in the vicinity between March and October 1994 and at the Newcastle site which was unduly influenced by local sources and was re-located in June 1994 to give more representative measurements of an urban background site.

As shown in Table 6.1, the annual mean concentrations of PM_{10} are relatively uniform across the country, lying between 20-34 µg/m³. From these data, there is a slight tendency for mean concentrations to be larger in regions with large traffic densities (eg London) or significant domestic coal burning (eg Belfast). The mean NO_x (nitrogen oxides) concentrations show a similar variation at these sites and the PM_{10}/NO_x ratio is relatively constant except at Belfast and Cardiff where the PM_{10} concentrations are relatively large. (See also Chapter 4).

In comparison with many of the influences described in the sections above, the influences of weather conditions tend to be more subtle. The passage of large scale weather systems causes day-by-day variations in most pollutants, PM_{10} included. If these weather systems are large enough and intense enough, then PM_{10} concentrations at several sites can apparently change simultaneously or with time lags of a few hours or less. Such events tend to be infrequent though and much of the variation in urban PM_{10} concentrations is driven by local variations in emissions and strong correlations are found with other urban pollutants.

A detailed study has been conducted of the correlations between the hourly PM_{10} concentrations measured at the AUN site in Edinburgh and the weather data for Edinburgh Airport for 1994. The analysis is summarised in Table 6.2, for the following hourly weather parameters:

- windspeed in knots,
- temperature in °C,
- rain in the last hour in 0.1 mm,
- sunshine intensity in W/m^2.

The analysis clearly shows that the correlations between PM_{10} and weather parameters tend to be weak and intensely seasonal. In the wintertime, PM_{10} concentrations appear inversely related to the windspeed. The greater the windspeed the lower the urban PM_{10} concentrations due to the effects of dilution and ventilation. In the summertime, this trend reverses and PM_{10} concentrations tend to increase with windspeed. There are two likely explanations for this phenomenon. The first is that wind-driven resuspension of surface dusts is greater in the dryer summer months. Secondly, at this coastal location, brisk sea breezes are common in the warmer hours of the day when traffic emissions of PM_{10} are highest..

Correlations with temperature show a similar seasonal turn-over from a wintertime inverse relationship to a summertime dependence. Winter days with strong PM_{10} concentration build-up tend to be those with colder mornings. During the summertime, PM_{10} concentrations build up during the day due to traffic activity and secondary particle formation takes place as temperatures rise giving an apparent association.

Rainfall could in principle exert a variety of impacts on PM_{10} concentrations. However, the Edinburgh data show that PM_{10} is inversely correlated with rainfall in the last hour during wintertime and positively correlated during summertime. In the wintertime, rainfall is associated with the passage of frontal systems with increased windspeeds and the general conditions under which urban pollutant build-up is not anticipated. Hence there appears to be a negative correlation between rain in the last hour and PM_{10} levels. In the summertime, rain tends to be more infrequent, more intense and has the potential to resuspend more material from the earth's surface when it falls.

Correlations of PM_{10} concentrations with sunshine intensity examine the relative diurnal profiles of PM_{10} and sunshine. As the mean diurnal curve of PM_{10} adjusts with season to reflect the changing balance of primary and secondary sources, then its correlation with sunshine hours alters. It is best in summer months when secondary paricles play a major role. This effect is illustrated in Table 6.2.

The cumulative distribution frequency of the PM_{10} concentrations observed at four of the sites operational in 1994 indicate that although there appears to be a degree of uniformity in the mean PM_{10} concentrations, differences are apparent when higher percentiles are considered as shown in Figures 6.10a to 6.10d. This reflects the impact that local sources or conditions can have on PM_{10} concentrations.

Further analysis and discussion on the PM_{10} measurements is given in subsequent sections of this and other Chapters in this report.

6.3.3 $PM_{2.5}$ Measurements

Although particulate matter is measured as PM_{10} at the national automatic monitoring sites, there is also an on-going measurement programme being undertaken at Hodge Hill in Birmingham by the City Council. The concentrations of $PM_{2.5}$, PM_{10} and black smoke are simultaneously being determined using two TEOM instruments with appropriate inlets and the smoke stain method respectively. The measurement site is about 70 metres south of an elevated section of the M6 motorway and the measurements have been made since October 1994. The data for the period from January to June 1995 indicate that the daily averages of $PM_{2.5}$, PM_{10} and black smoke lie between 2-60 µg/m^3, 4-76 µg/m^3 and 1-41 µg/m^3 respectively, as shown in Table 6.3 (Appleby, 1995). The concentrations of $PM_{2.5}$ are always lower than those of PM_{10}, varying between 28 to 100% with an average value of 60%. The variation appears to be weather dependent. (See also Chapter 8).

6.3.4 Strong Acid Aerosol Measurements

Strong acid aerosol was measured on a daily basis in London between 1963 and 1972 by the MRC Air Pollution Unit based at St Bartholomew's Hospital. Earlier measurements (from 1957) had only been made during pollution episodes. Samples were collected on filter paper and the total acidity determined by back titration following the addition of sodium tetraborate. The acidity was assumed to be solely due to sulphuric acid. Table 6.4 gives a summary of the measurements made during this period (MAAPE, 1992). The highest daily mean level of H_2SO_4 recorded was 134.1 µg/m^3 in 1964 which can be compared with the highest daily and hourly levels of 347 and 678 µg/m^3 respectively which were recorded during the December 1962 episode. The

Figure 6.10a London Bloomsbury PM_{10} Cumulative Frequency Distribution Plot (Hourly Averages).

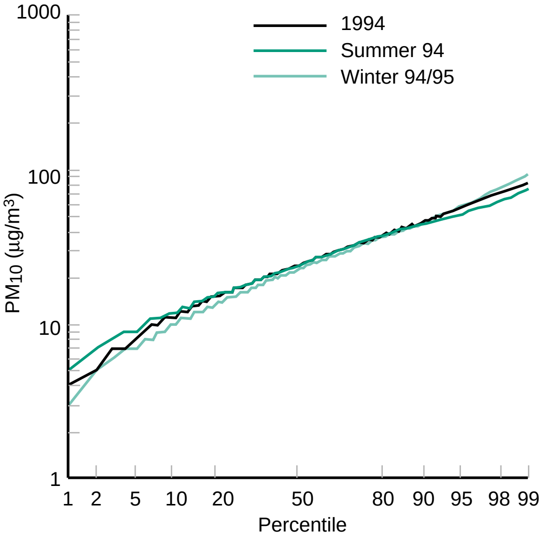


Figure 6.10b Belfast Centre PM_{10} Cumulative Frequency Distribution Plot (Hourly Averages).

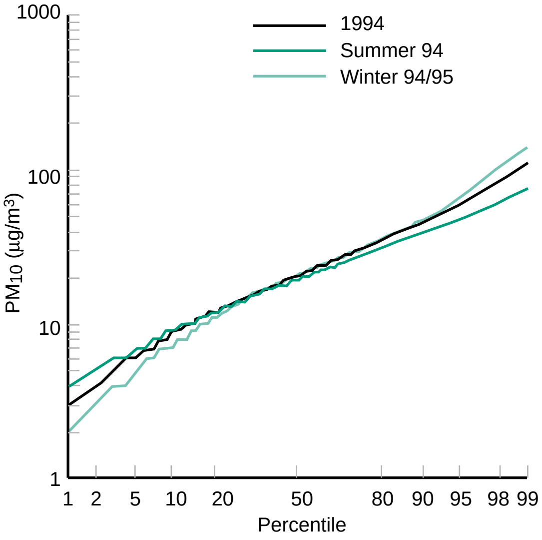


Figure 6.10c Birmingham Centre PM_{10} Cumulative Frequency Distribution Plot (Hourly Averages).

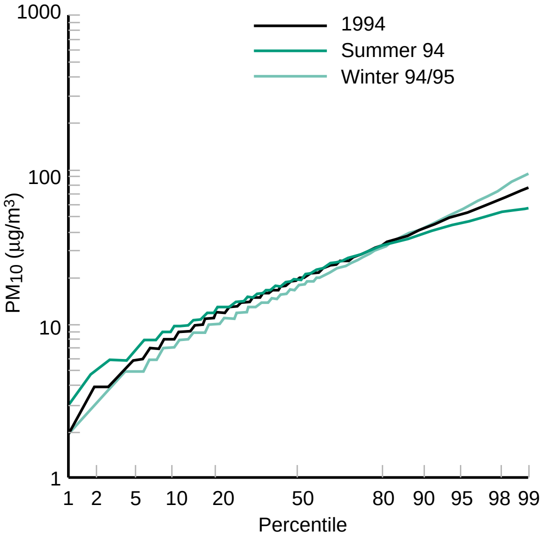


Figure 6.10d Birmingham East PM_{10} Cumulative Frequency Distribution Plot (Hourly Averages).

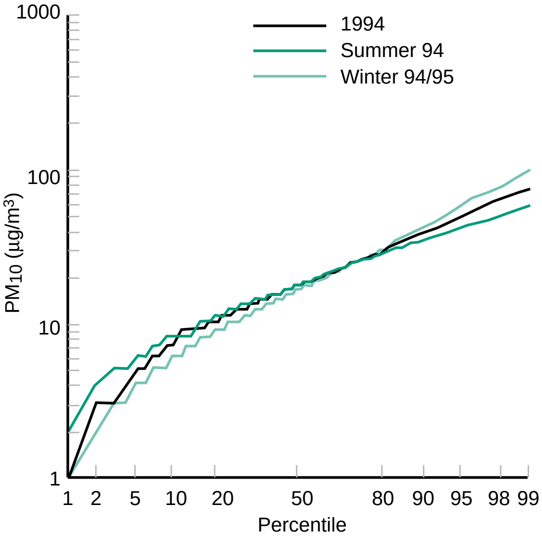


table shows that between 1964 and 1972 H_2SO_4 concentrations fell by more than 50%.

Sulphuric acid concentrations showed a smaller winter to summer ratio than those observed for sulphur dioxide and other primary pollutants. The ratio indicated that there was a significant source in the summer and two distinct production mechanisms were identified. The photochemical nature of one of the production mechanisms was clearly illustrated by the strong correlation observed between total particulate sulphate and ozone measurements made in central London during a photochemical episode in June 1989. (MAAPE, 1992).

Concentrations of sulphuric acid tend to be lower in rural areas but are harder to interpret reliably because of the interference from ammonia to form ammonium sulphate either in the atmosphere or during sampling and subsequent analysis. One of the few direct

Table 6.3 Comparison of Monthly Average Measurements of Black Smoke, $PM_{2.5}$ and PM_{10} made at Birmingham, Hodge Hill for January to June 1995 (Appleby, 1995).

Month	**Average Monthly Value**			**Ratio***		
	Smoke (µg/m^3)	**$PM_{2.5}$** (µg/m^3)	**PM_{10}** (µg/m^3)	**Smoke:$PM_{2.5}$**	**Smoke:PM_{10}**	**$PM_{2.5}$:PM_{10}**
January	9	11	15	0.80	0.56	0.70
February	4	11	17	0.31	0.21	0.64
March	7	12	22	0.48	0.29	0.60
April	5	15	28	0.34	0.19	0.57
May	6	15	26	0.38	0.20	0.56
June	6	11	24	0.59	0.27	0.48
Minimum Daily Value	1	3	4	0.07	0.04	0.3
Maximum Daily Value	41	43	66	1.72	1.45	1.0
Mean Value	6	13	22	0.48	0.29	0.60

* Mean value of ratios determined for each day in that month,

Table 6.4 Historical London Daily Acid Aerosol Concentration (µg/m^3 of total H^+ as H_2SO_4) (MAAPE, 1992).

Year	**Annual**			**Winter***		
	Mean	**S.D.**	**Max.**	**Mean**	**S.D.**	**Max.**
1964	6.8	9.6	134.1	10.4	15.5	134.1
1965	5.1	3.4	26.3	7.3	5.0	42.2
1966	4.6	3.2	24.3	7.5	4.1	24.3
1967	4.1	2.9	20.2	5.2	2.7	22.5
1968	4.5	2.9	25.3	7.6	3.9	25.3
1969	4.3	3.0	19.0	6.0	3.2	17.0
1970	3.0	2.5	18.2	4.8	2.9	19.0
1971	3.2	2.7	29.7	3.3	3.7	29.7
1972	3.2	2.7	22.9	4.5	2.4	13.7

(*) The winter period is from 1st November of the preceding year to 28th or 29th February of the year shown.

measurements was when simultaneous measurements were made at 3 sites in Essex over 33 days between 1987 to 1989 (Kitto and Harrison, 1992). The measurements gave mean H^+ ion concentrations between 11.5 to 28.7 neq/m^3, equivalent to 0.6-1.4 µg/m^3 of H_2SO_4. Approximate H^+ ion concentrations have also been inferred from the extended series of measurements of sulphate, nitrate and ammonium made at Harwell assuming ionic balance (i.e. $H^+ = (SO_4^{2-} + NO_3^-) - NH_4^+$ in equivalence units) (MAAPE, 1992; Lee and Derwent, 1995). A simple regression analysis suggested a downward trend in the H_2SO_4 concentration with absolute concentrations in 1991 between 3-5 µg/m^3. The Harwell measurements are discussed further in section 6.3.6. Although the concentrations observed in Essex were lower than those inferred from the Harwell dataset, this is consistent with the higher NH_3 concentrations expected in Essex.

6.3.5 Other Urban Measurements of Particulate Matter

As part of the London Air Quality Network run on behalf of London Boroughs by the South East Institute of Public Health, TEOM instruments have been set up to measure PM_{10} concentrations at a number of sites across London: Bexley, Greenwich, Haringey, Kensington and Chelsea, Sutton, Tower Hamlets and Thurrock. The site at Bexley is an affiliated site in the national urban network although particulate matter was measured as total suspended particulate prior to affiliation. Data for the sites operational in 1994 (at Bexley, Greenwich and Tower

Table 6.5 1994 Statistics for PM_{10} from the Sites in the London Air Quality Network.

Site	**Bexley**	**Greenwich**	**Tower Hamlets**
Site Type	**SB**	**SB**	**UB**
Number of Days Operational	197	321	340
Number of Days on which daily mean levels of PM_{10} (µg/m³) exceeded			
10	188	302	329
20	116	144	194
30	59	51	96
40	33	18	47
50	8	4	12
60	2	4	5
70	1	2	4
80	0	1	1
90	0	0	0
100	0	0	0
Annual Mean Concentration (µg/m³)	25	21	26

Notes: SB - suburban background; UB - urban background. Data from Greenwich and Tower Hamlets are provisional

Table 6.6 Provisional Statistics for PM_{10} from the Roadside Sites in the London Air Quality Network and the National Automatic Urban Monitoring Sites in London for January to June 1995.

Site	**London Bloomsbury**	**London Bexley**	**Haringey**	**Thurrock**
Site Type	**UB**	**SB**	**R**	**UB**
Average PM_{10} Concentration (µg/m³)	26	22	22	24
Maximum Hourly PM_{10} Concentration (µg/m³)	249	173	130	108
Number of Days on which Daily Mean Level of $PM_{10} \geq 50$ µg/m³	9	8	6	5
Data Capture %	96	97	91	51

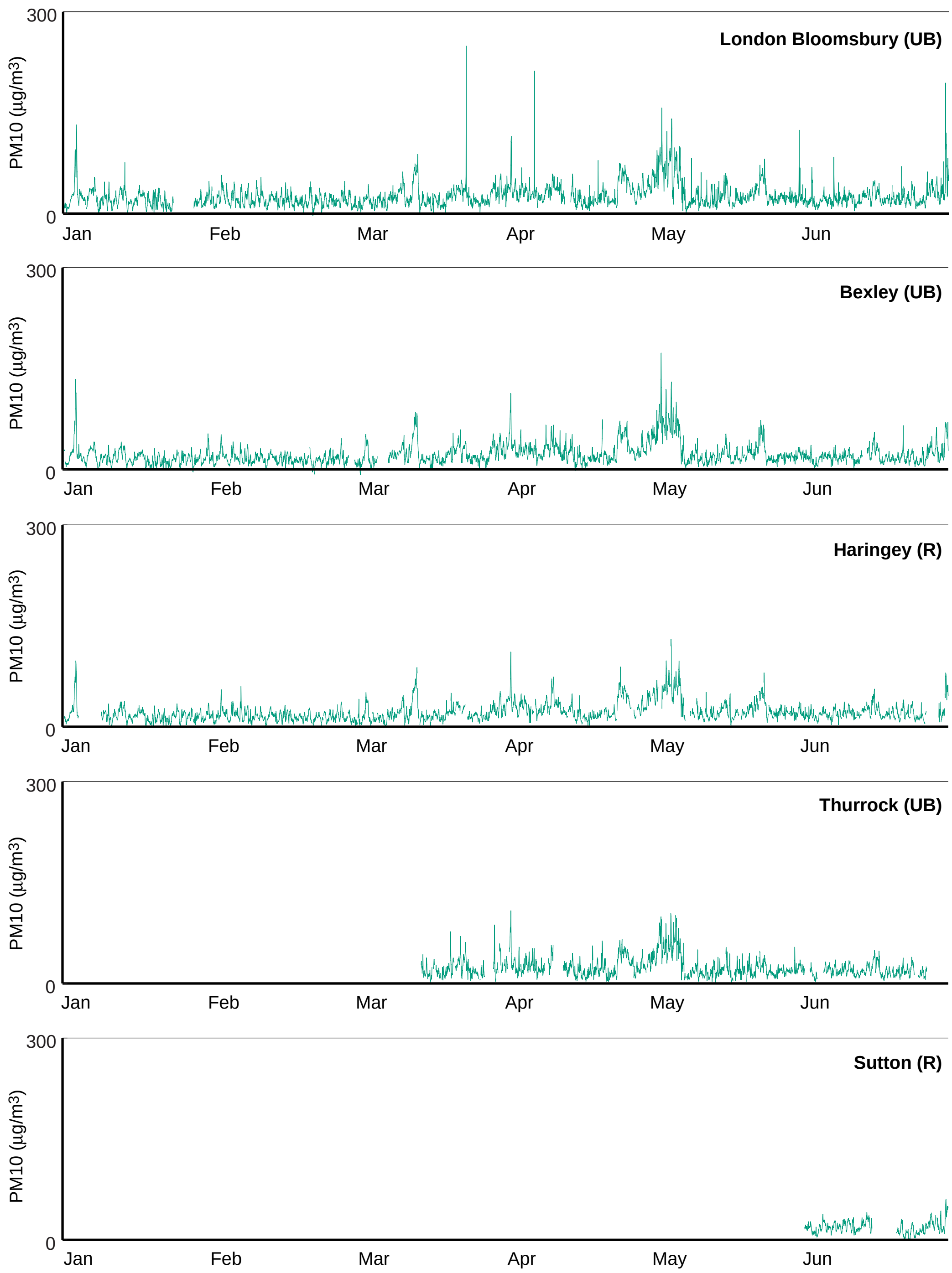
Notes: (1) Site types: R - roadside; SB - suburban background; UB - urban background.
(2) The Thurrock site became operational in March 1995.

Hamlets) are summarised in Table 6.5. The annual mean concentrations of 25, 21 and 26 µg/m³ recorded respectively at the three sites are comparable to the PM_{10} concentrations observed at the urban background sites in the national urban monitoring network.

Two of the sites in the network at Haringey and Sutton are situated in roadside locations. The measurements made at these sites and also at Thurrock for the period from January to June 1995 are presented in Figure 6.11 and are compared in the same Figure with the measurements made at the national sites at London Bexley and Bloomsbury over the same period. The mean and maximum hourly concentrations recorded at certain of these sites between January and June 1995 are given in Table 6.6. The Sutton site only became operational in June 1995. The concentrations observed at the roadside sites are thus far comparable to those measured at the urban background sites during this period.

Other roadside measurements have clearly demonstrated an elevation in PM_{10} concentration close to road traffic. Figure 6.12 shows a time series of PM_{10} measurements made by Westminster City Council at Marylebone Road and Oxford Street in

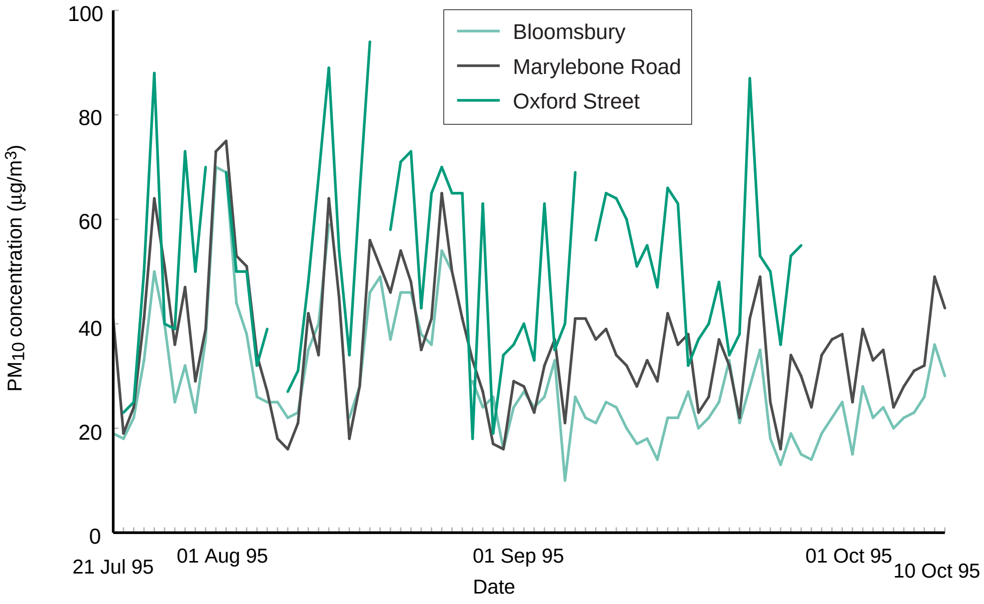
Figure 6.11 Roadside PM_{10} Data from London Compared to Urban Background PM_{10} Measurements.



Note: UB = Urban Background
R = Roadside
Data for roadside stations provided by SEIPH
Data for London Bloomsbury and Bexley are provisional.

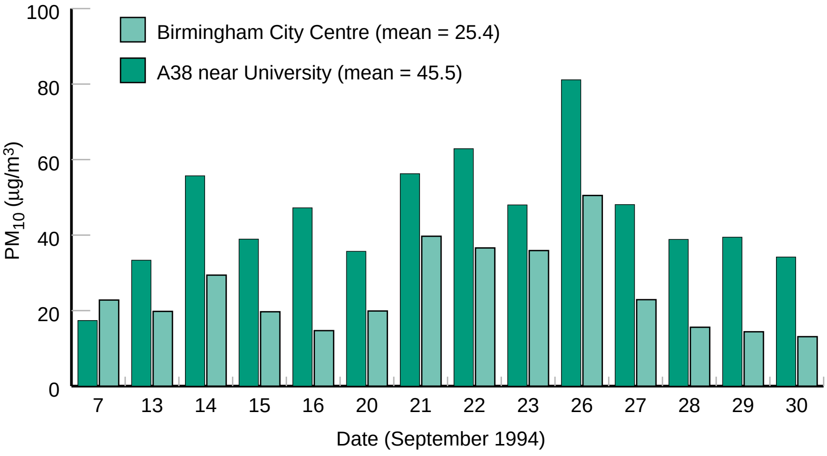
Central London using TEOM instruments, compared with the AUN site at London, Bloomsbury. The highest concentration over the period monitored was at the Oxford Street site (mean = 52 µg/m³), compared with 36 µg/m³ at Marylebone Road and 29 µg/m³ at Bloomsbury. Oxford Street is notable for being restricted to buses and taxis only. Marylebone Road appears similar to Bloomsbury for the period 21st July to 1st September, when traffic is reduced due to summer holidays. In September and October it shows

Figure 6.12 Hourly-mean Concentrations of PM_{10} at Roadside and Urban Background Sites in London, July to October 1995.



Source: Westminster City Council, 1995.

Figure 6.13 Eight-hourly Concentrations of PM_{10} at Roadside and Background Sites in Birmingham.



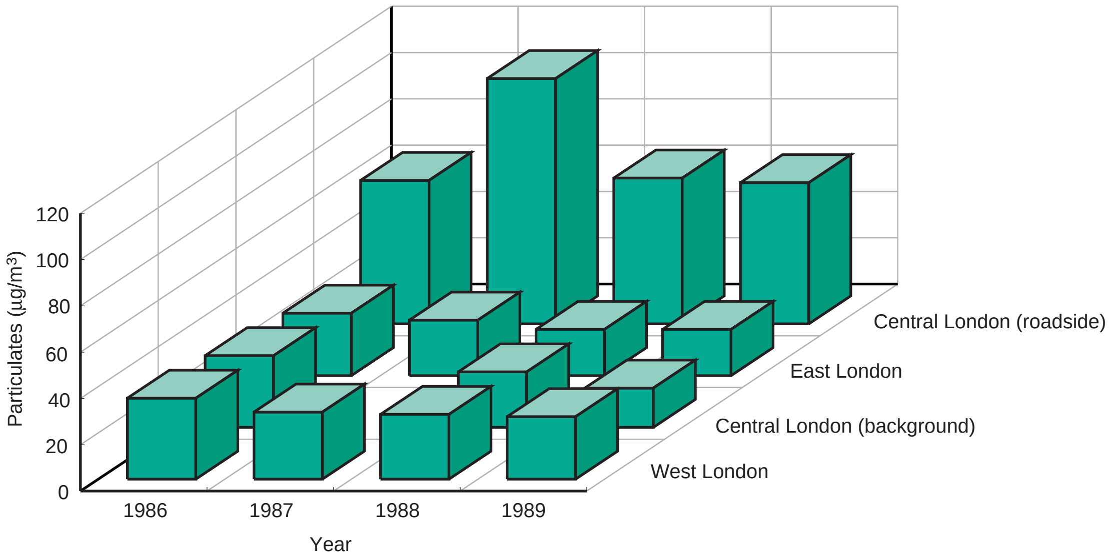
Source: Jones and Harrison, 1995.

a clear elevation, typically by 10-20 µg/m^3 above concentrations at the Bloomsbury site.

Eight-hourly daytime measurements of PM_{10} have also been made on the busy A38 road in Birmingham, and compared with data collected simultaneously from the urban background AUN site at Birmingham, Centre. The data (Figure 6.13) show a clear elevation at the roadside site (mean = 45.5 µg/m^3) over the background site (mean = 25.4 µg/m^3) consistent with that observed for Marylebone Road and Oxford Street in London.

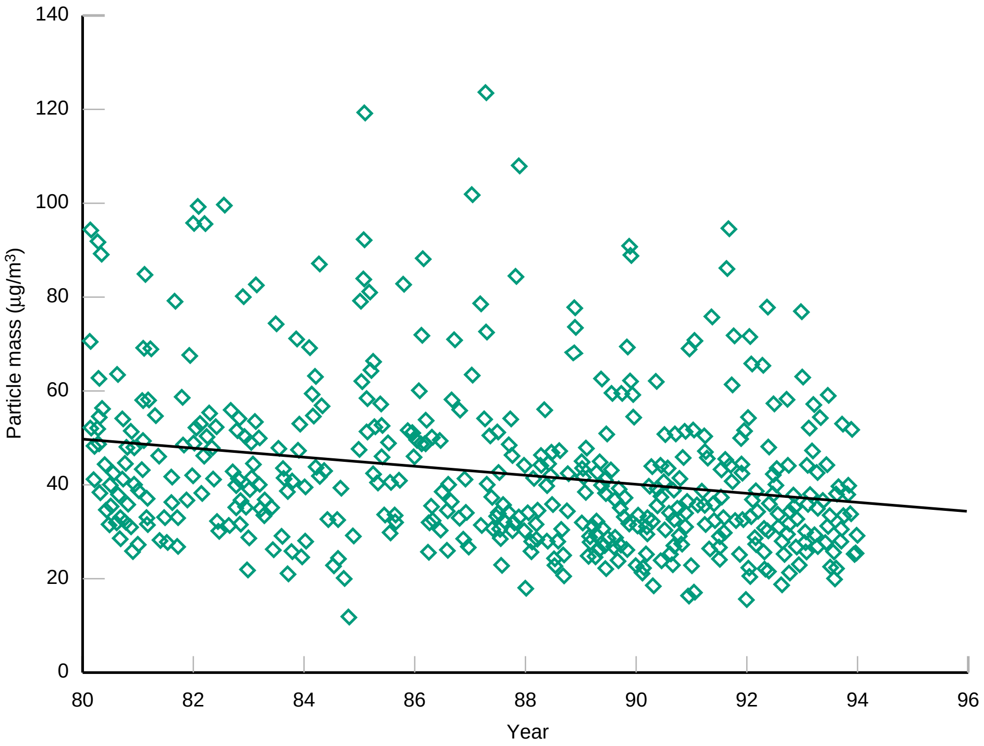
The former London Scientific Services measured concentrations of airborne particulate matter at four sites in London using M-type samplers, with subsequent gravimetric analysis of the particulate matter (QUARG, 1993a). This sampler has a particle size cut-off of approximately 10 to 15 µm (see Chapter 3) and, depending on the wind speed may

Figure 6.14 Annual Mean Concentrations of Suspended Particles at Four Sites in London (1986-1989).



Source: LSS, 1989.

Figure 6.15 Trends in Weekly-mean Suspended Particle Concentrations, Manchester 1980-93.



Source: Miller and Lewis, 1996.

therefore tend to under or overestimate PM_{10} concentrations. The samplers were located at three background and one roadside site. The measurements made are summarised in Figure 6.14. The levels measured at the roadside were 2.5 to 3 times higher than those at the background locations, indicating the importance of road traffic as a source of particulate matter. The apparent downward trend for the background locations was believed to be real as other pollutants measured at these sites did not show any significant trend over the period.

An extended series of measurements of suspended particulate matter using M-type samplers was made at Piccadilly Gardens in central Manchester between 1980 and 1993 (Miller and Lewis, 1996). The measurements showed a very strong seasonal behaviour. The dataset was corrected for the seasonal effect and an underlying decline in particulate matter of about 1 µg/m^3 per year was observed (Figure 6.15). During 1987 and 1988, a series of measurements was made using an 8-stage Andersen cascade impactor. A pre-separator was used to remove particles with sizes greater than 13.5 µm. The highest concentration was observed for the size range of less than 2 µm with a median value of 1.2 µm. Unfortunately these measurements were not repeated to identify trends in the size distribution.

The national multi-element survey has also shown that the concentration of a range of elements, averaged over the 5 monitoring sites, has fallen considerably over the 17 years of operation of the survey (Loader, 1994).

6.3.6 Rural Measurements of Particulate Matter

Black smoke measurements were made at a number of rural locations as part of the smoke and sulphur dioxide network until 1991. Figure 6.16 shows the annual mean concentrations of black smoke recorded at 4 sites in the network: Caenby, Husborne Crawley, Ratcliffe and Camborne. Although the decline in smoke levels was not as dramatic as those observed at urban sites, there has still been a fivefold reduction between the early 1960s and 1991. The annual mean concentrations recorded in 1990 at the Caenby, Husborne Crawley, Ratcliffe and Camborne sites were 7, 8, 11 and 3 µg/m^3 respectively. The values at the urban sites in Belfast, Stoke-on-Trent, Lambeth and Norwich were 17, 19, 25 and 12 µg/m^3 respectively. The ratio of urban to rural smoke levels has fallen substantially over this period so that urban levels are now closer to those recorded at rural sites.

A campaign to measure particulate matter concentrations in rural areas was undertaken by TBV Science over a three month period between July and September 1994. Sampling was carried out at 6 sites in the rural West Midlands area using M-type samplers. The average concentrations recorded over this period at the different sites were found to lie between 11 and 20 µg/m^3.

A study has recently been undertaken to compare concentrations of PM_{10} at a rural site near Bristol, Chew Lake, with those observed at the national monitoring sites at Bristol and Cardiff (International Mining Consultants Limited, 1995). The monitoring site was chosen to be representative of rural background concentrations and was therefore sited away from any major industrial or local pollution sources. PM_{10} measurements were made using a TEOM instrument for one month between 24 January and 21 February 1995. Figure 6.17 shows the 30 minute mean PM_{10} measurements made at Chew Lake, Bristol and Cardiff during this period. Although there are periods when concentrations of PM_{10} were elevated at the urban sites, these are not apparent in the rural measurements. The rural concentrations were generally low primarily as a result of the wind blowing mainly from the west during the measurement period. The mean concentration of PM_{10} measured during this period was 14 µg/m^3 at Chew Lake, 20 µg/m^3 for the Bristol site and 23 µg/m^3 at the Cardiff site. Further analysis of the measurements led the authors of the study to conclude that rural particulate matter consists of several different components and ashing of representative samples indicated that the component attributable to vehicle exhaust was no greater than 30%. These conclusions are tentative given the limited monitoring period of the study.

There are various other networks from which data on particular chemical constituents in particulate matter (e.g. Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-} and NO_3^-) are available. These data can be used to infer the total particle mass. None of these measurements have used inlets designed to sample a defined size fraction. However, like the M-type sampler, the methods used tend not to sample large particles efficiently.

Figure 6.16 Annual Arithmetic Mean Concentrations of Smoke at Rural Sites.

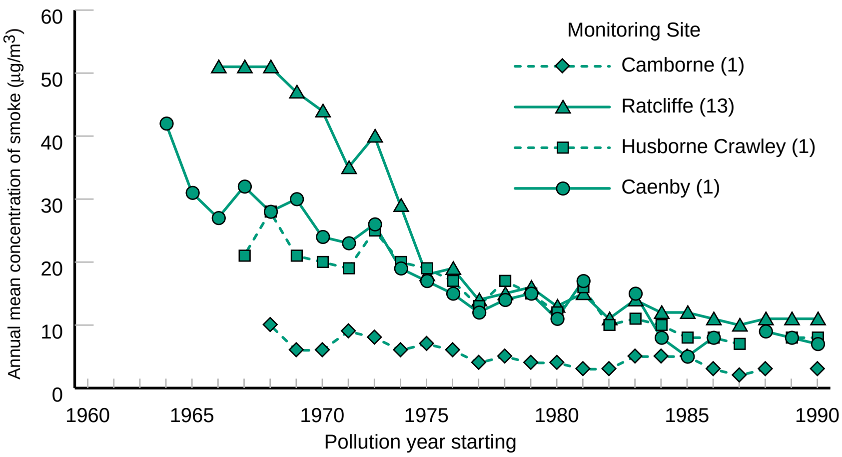
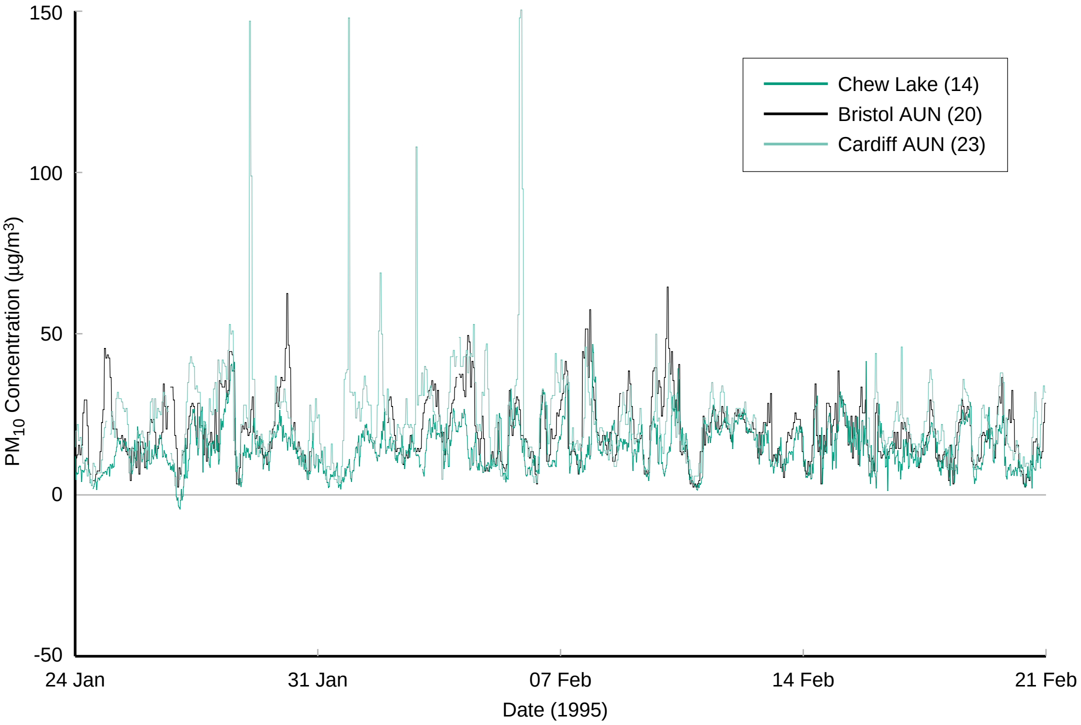


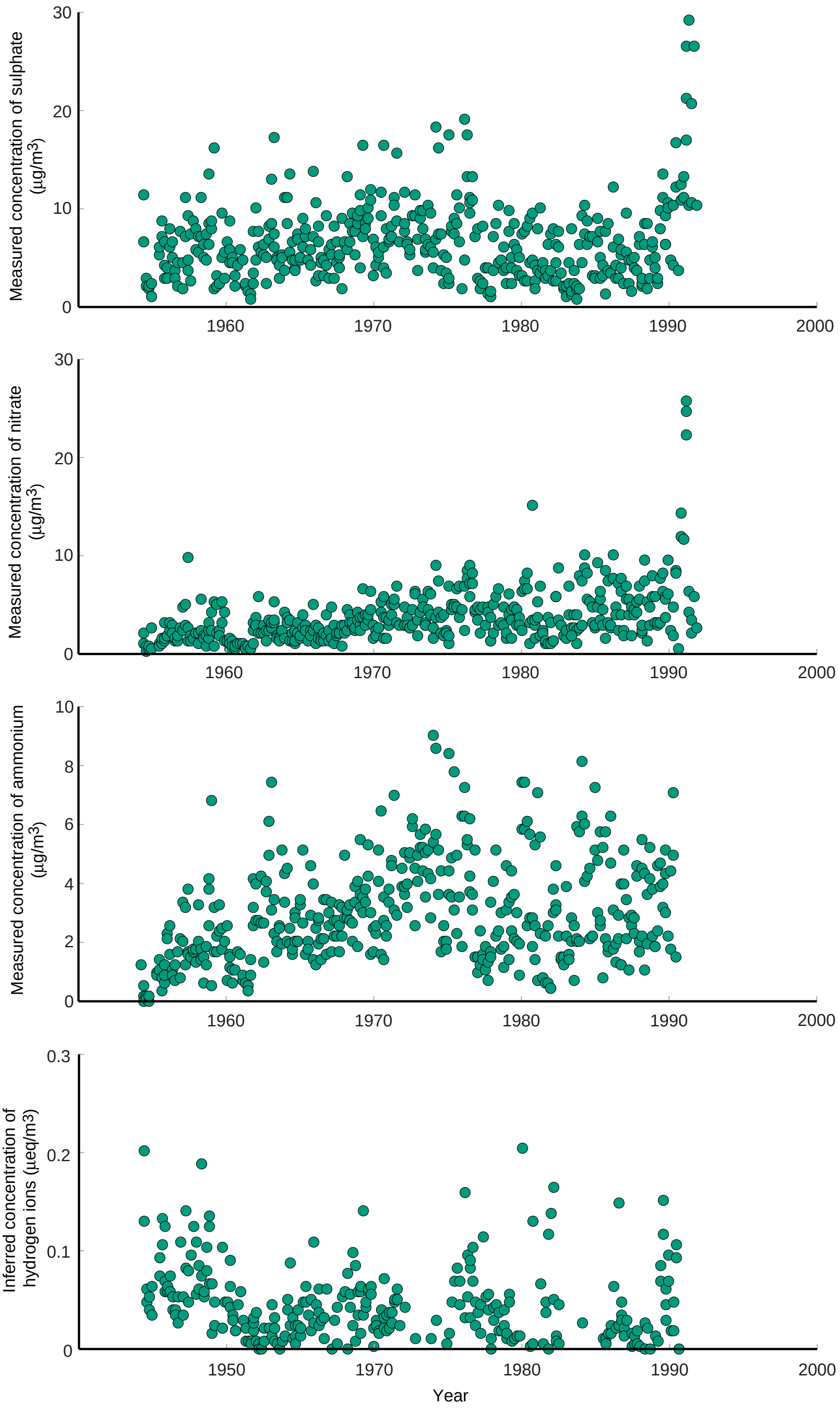
Figure 6.17 30 Minute Mean PM_{10} Concentrations at Chew Lake compared with Bristol and Cardiff.



Note: Data for Bristol and Cardiff are provisional.

At Chilton (SU 472854) in Oxfordshire, measurements of particulate sulphate, nitrate and ammonium have been carried out using a filter sampler since 1954 as shown in Figure 6.18 (Lee and Derwent, 1995). Between 1954 and 1975 the mean concentration of particulate sulphate increased from around 6 $\mu g/m^3$ to 8 $\mu g/m^3$ while that of particulate nitrate increased from 1.5 $\mu g/m^3$ to 4.5 $\mu g/m^3$. By the 1990s, the mean concentration of particulate sulphate had decreased to 4 $\mu g/m^3$ and that of particulate nitrate had increased to 5 $\mu g/m^3$. The total mass of ammonium nitrate and ammonium sulphate present at this site can be calculated if it assumed that the counter cation for the nitrate and sulphate is only ammonium. This suggests that the present concentration is approximately 12 $\mu g/m^3$ which has fallen from a value of 16 $\mu g/m^3$ in the mid 1970s.

Figure 6.18 Chilton Time Series Measurements of SO_4^{2-}, NO_3^-, NH_4^+ and Inferred H^+.



Note: Sampling durations are not constant throughout the programme.

Eskdalemuir (NT 235030) in Scotland and High Muffles (SE 776939) in North Yorkshire are more remote sites at which particulate sulphate and the sum of nitric acid and particulate nitrate have been measured since the late 1980s. Since the mean nitric acid concentration is small, these data can also be used to infer the total mass of ammonium sulphate and ammonium nitrate. At Eskdalemuir, the total mass is around 6 µg/m^3 and at High Muffles, the total mass is approximately 11 µg/m^3. (See also Chapter 8).

There are also three other rural sites at which the concentrations of sodium, chlorine, calcium and magnesium have been measured (Lee, Espenhahn and Baker, 1995). From these measurements the contribution of these elements to the mass of particulate matter can be inferred. The current concentration at sites in England is between 1.5 to 3 µg/m^3.

At none of the sites discussed above have all the components of particulate matter been measured. However, the total particulate mass can be estimated very approximately by combining the measurements of black smoke, particulate ammonium, sulphate, nitrate, sodium, chlorine, calcium and magnesium. A current value of 20 µg/m^3 can be inferred for rural areas in central southern England which is larger than the gravimetric measurements described above but within the errors involved in inferring the total mass from the individual components.

6.4 CORRELATION BETWEEN DIFFERENT MEASURES OF PARTICULATE MATTER

Particulate matter is characterized by the measurement method used and numerous studies have been undertaken to compare the measurements made by the different monitoring techniques. This is particularly important when investigating the potential health effects arising from airborne particulate matter. A common basis is needed so that results obtained using one measurement technique can be compared directly with the results from other instruments.

6.4.1 Correlation Between Black Smoke and Total Suspended Particulate Matter

A significant number of intercomparisons have been undertaken to relate particulate measurements made using the smoke stain and gravimetric methods (see references in Ball and Hume, 1977; Bailey and Clayton, 1980). The general conclusion of these studies was that the two measures of particulate matter were highly correlated but that the regression coefficients were site specific.

A study was undertaken from County Hall in London to measure the levels of black smoke and total suspended particulate matter (Ball and Hume, 1977). The concentration of airborne lead was also determined by analysing the suspended particulate matter collected. The measurements were made during the period from May 1975 to April 1976 and were used to infer that the vehicular contribution to the annual mean dark smoke concentration was about 77%. Daily mean levels of black smoke and particulate matter were determined four times during each working week.

The measurements of total suspended particulate were generally higher than the corresponding levels of black smoke with closer agreement in winter or during pollution episodes. The ratio of black smoke to total suspended particulate matter varied from approximately 1/6 to 1/1. Regression analyses showed statistically significant seasonal changes but these changes were not regular as might be expected if the particulate matter arose from space heating emissions. The absence of a correlation between the ratio of the black smoke concentration to total suspended particulate matter concentration against the number of degree days per day when the temperature was below 15°C provided further confirmation that the black smoke arose from vehicular rather than space heating sources.

The seasonal and annual mean levels are summarised in Table 6.7. The correlation between black smoke and lead was very strong ($r^2 = 0.96$) and the relationship held for all seasons and for different meteorological conditions. The dominant source of lead was from road traffic indicating that a large fraction of the black smoke also arose from road traffic emissions.

6.4.2 Correlation Between PM_{10} and Black Smoke

A number of studies have recently been undertaken to investigate the correlation between the concentrations of PM_{10} and black smoke to see whether the more extensive database available and the on-going measurement programmes of black smoke could be used to infer PM_{10} concentrations.

Table 6.7 Seasonal and Annual Mean Concentrations of Black Smoke, Total Suspended Particulate Matter and Airborne Lead (in µg/m^3) as Measured at County Hall, London (Ball and Hume, 1977).

Period	Black Smoke	TSP	Airborne Lead
Summer	30	77	0.50
Winter	59	108	1.06
Annual	45	93	0.78

PM_{10} concentrations at the automatic monitoring sites operational in the pollution year 1992/93 were compared with black smoke recorded at the nearest smoke and sulphur dioxide network site. The regression analysis of the daily mean concentrations of PM_{10} and black smoke indicated that the correlation is no stronger than that observed for PM_{10} with other pollutants, as shown in Table 6.8. The correlation between daily mean PM_{10} and black smoke is however stronger in the winter than in the summer, indicating the larger contribution of motor-vehicle derived PM_{10}

Table 6.8 Correlations Between PM_{10} and Other Pollutants Including Black Smoke. Daily Averages for Pollution Year 1992/93.

Site	Period	Ozone	NO_x	NO	NO_2	CO	SO_2	SO_2 by Net Acidity Method	Black Smoke
London	summer 92	0.25	0.68	0.45	**0.88**	0.45	0.73	0.58 #	0.68 #
(2.3 km)	winter 92/93	-0.25	0.71	0.71	0.59	0.56	0.62	0.59	**0.79** #
	year 92/93	0.08	0.59	0.52	0.73	0.49	0.62	0.58	0.69 #
Edinburgh	summer 92	-	-	-	-	-	-	-	-
(0.4 km)	winter 92/93	-0.53	0.67	0.66	0.62	0.61	0.62	0.32	0.46 #
	year 92/93	-0.53 #	0.68 #	0.68 #	0.65 #	0.61 #	0.62 #	0.32 #	0.46 #
Cardiff	summer 92	0.09 #	0.36	0.26	0.44	0.40	0.42	0.24	0.70
(1.2 km)	winter 92/93	-0.34	0.57	0.56	0.46	0.40	0.54	0.27	0.42 #
	year 92/93	-0.25	0.58	0.56	0.48	0.45	0.56	0.15	0.53 #
Belfast	summer 92	-0.20	0.71	0.59	0.68	0.57	0.65	0.34	0.34
(0.3 km)	winter 92/93	-0.42	**0.87**	**0.88**	0.69	**0.90**	**0.86**	0.63	0.73 #
	year 92/93	-0.40	**0.85**	**0.84**	0.65	**0.85**	**0.85**	0.64	0.71 #
Birmingham	summer 92	-0.08	0.74	0.61	**0.82**	0.63	0.71	0.66	0.69 #
(5.5 km)	winter 92/93	-0.42	0.58 #	**0.88**	0.65 #	**0.88**	**0.87**	0.73	**0.90** #
	year 92/93	-0.23	0.70 #	**0.76**	**0.78** #	0.74	**0.79**	0.69	0.74 #
Newcastle	summer 92	-0.11	0.59	0.46	**0.77**	0.57	0.51	0.25	0.54 #
(0.1 km)	winter 92/93	-0.56	**0.76**	0.70	**0.78**	0.56	0.61	0.43	**0.77** #
	year 92/93	-0.33	0.64	0.56	**0.75**	0.55	0.55	0.34	0.63 #

Notes (1) Black Smoke from national survey sites; (2) The distances between the PM_{10} and black smoke sites are given beneath the site name; (3) Numbers are highlighted where the correlation is greater than 0.75; (4) # indicates that the data capture rate is less than 50%.

Figure 6.19a Daily-average PM_{10} and Black Smoke at Bloomsbury AUN site, April 1994 to March 1995.

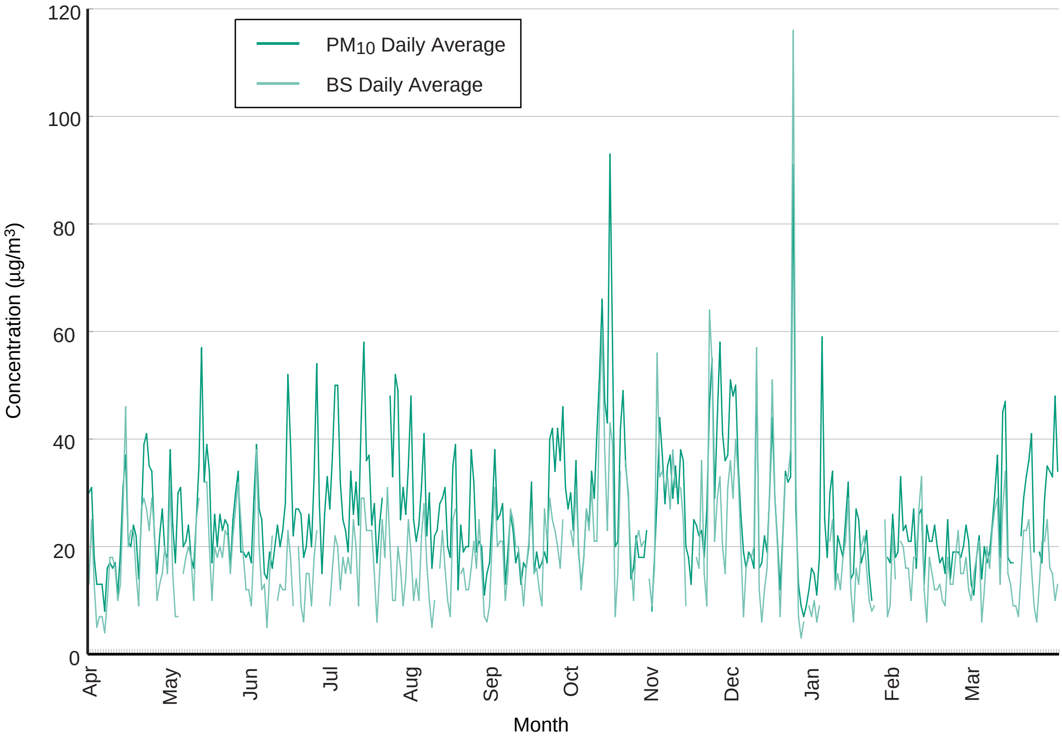
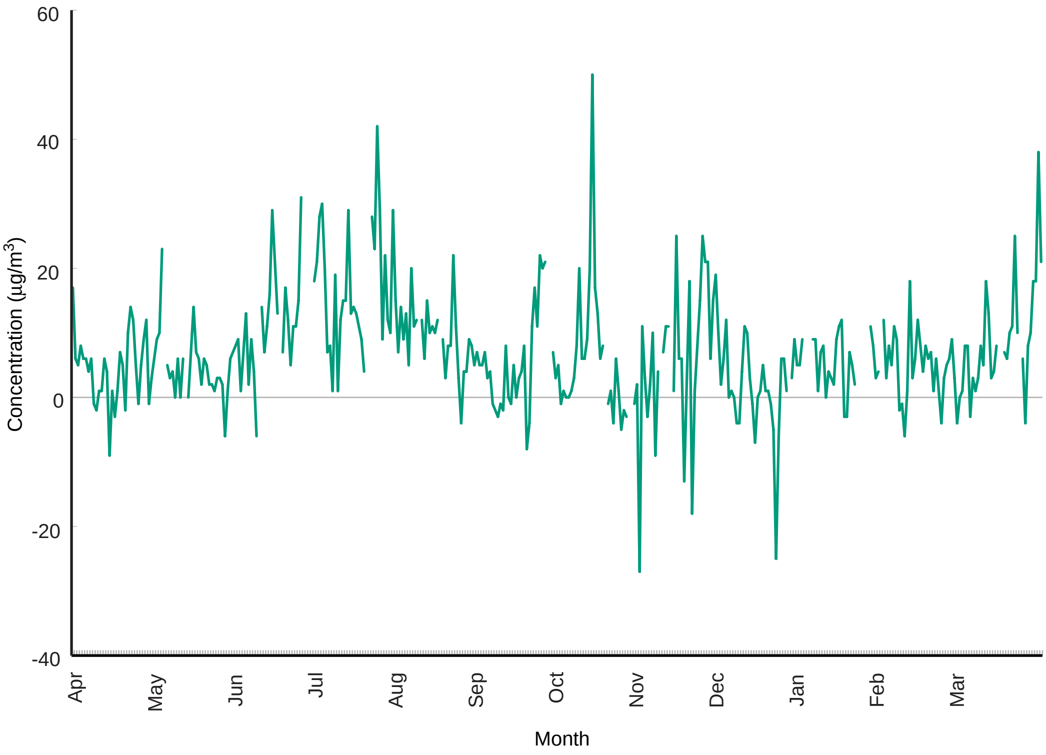


Figure 6.19b Daily-average (PM_{10} - Black Smoke) at Bloomsbury AUN Site, April 1994 to March 1995.



Note: Data for 1995 are provisional.

in the winter and the contribution of secondary PM_{10} to the summer concentrations.

This work has been extended by measuring PM_{10} and black smoke concentrations at 3 co-located sites in Belfast (Centre), Birmingham (Centre) and London (Bloomsbury) between April 1994 and March 1995 (Loader, 1995). The results indicate that the 24-hour average PM_{10} concentrations are generally higher than those of black smoke and the two pollutants generally rise and fall together as shown in Figure 6.19a for the London Bloomsbury site. A plot of the difference between PM_{10} and black smoke shows a seasonal variation (Figure 6.19b). PM_{10} concentrations are systematically higher in the summer with comparable concentrations of both pollutants in the wintertime, and occasionally episodes when the black smoke exceeds the PM_{10}. Analysis of the data indicates that the two pollutants are correlated. The correlation was again stronger for the wintertime period than for the summertime at all sites but the regression coefficients, given in Table 6.9, show significant variation from site to site. These results are consistent with a larger fraction of the particulate matter in the summertime being of secondary origin with different optical properties (since it contains a greater proportion of lighter coloured material) than the particulate matter generated in the wintertime, which is more likely to arise from road traffic. The differences between sites reflect the contributions of the various sources to the observed concentrations of particulate matter. This is not surprising given the nature of the emission sources present in these cities. Further work is needed to determine whether the relationships identified so far hold for other urban environments with similar emission patterns.

Similar conclusions were reached when PM_{10} measurements made at the national monitoring site in Bristol were compared with average concentrations of black smoke measurements made at 6 other sites in the Bristol conurbation during 1993 (Muir and Laxen, 1995). The study again found a strong seasonal effect on the relationship between PM_{10} and black smoke. PM_{10} concentrations were generally higher than those of black smoke. A regression analysis of the daily mean PM_{10} on black smoke gave a slope of 3.7 for the summertime data and 2.0 for the wintertime data. Black smoke concentrations increased in wintertime and these changes were not apparent in the PM_{10} record. The study concluded that the black smoke measurements referred to a different sub-set of the airborne particulate matter to that being sampled by the TEOM instruments.

6.5 BEHAVIOUR OF PARTICULATE MATTER CONCENTRATIONS

6.5.1 Correlation With Other Pollutants

In the first QUARG report (QUARG, 1993a), a regression analysis of the PM_{10} and carbon monoxide monitoring data suggested that there was a weak correlation between the two pollutants. Since then, the relationship between PM_{10} and other pollutants such as ozone, nitrogen oxides and benzene has been investigated by a number of workers

Table 6.9 Linear Regression Analysis of Co-located Black Smoke and PM_{10} Measurements Made at Three Sites between April 1994 and March 1995 (Loader, 1995).

Site	**Summer (Apr-Sep)**		**Winter (Oct-Mar)**		**Annual (Apr-Mar)**	
	Slope	**Intercept**	**Slope**	**Intercept**	**Slope**	**Intercept**
Belfast (Centre)	0.54	-1.30	1.29	-14.1	1.19	-13.7
			0.83 *	-3.14 *	0.76 *	-3.81 *
Birmingham (Centre)	0.45	+0.86	1.17	-10.4	0.97	-8.99
			0.97 *	-6.54 *	0.79 *	-5.04 *
London (Bloomsbury)	0.42	+6.87	0.80	-0.18	0.67	1.85

(*) Regression analysis with outliers excluded from the analysis.
Note: Regression of black smoke on PM_{10}.
PM_{10} data for 1995 are provisional.

Figure 6.20 Monthly Regressions of PM_{10} and CO on Hourly Data Points.

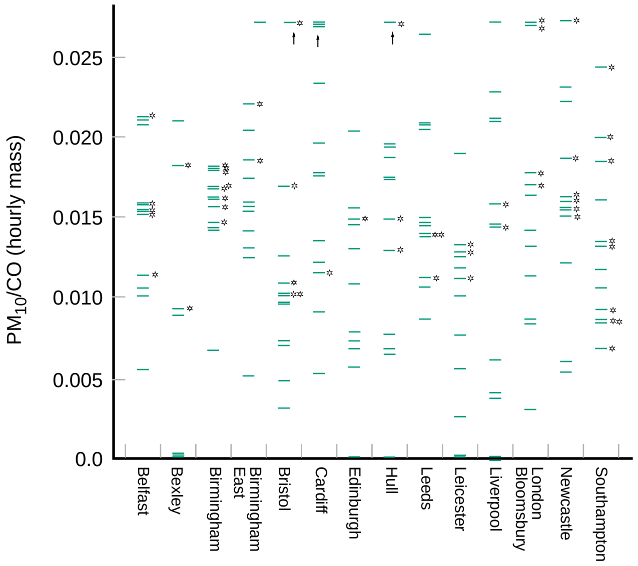
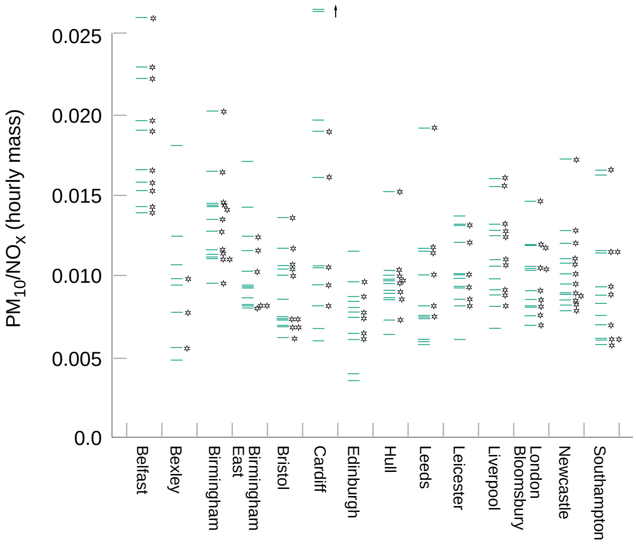


Figure 6.21 Monthly Regressions of PM_{10} and NO_x on Hourly Data Points.



Note: Based on provisional data.

- to define relationships between PM_{10} and pollutants which could be used to infer ambient concentrations of PM_{10} in the absence of direct measurements

- to use the relationship between pollutants to establish sources and to estimate the contribution made by these sources to ambient concentrations.

The latter point is discussed in other Chapters of this report.

The daily-averaged concentrations of the pollutants recorded at the urban automatic monitoring sites together with the measurements of acidity and black smoke from the nearest national smoke and SO_2 network site have been analysed for the pollution year 1992/93. The correlation coefficients derived for the relationship between PM_{10} and the other pollutants (O_3, NO, NO_2, NO_x, CO, SO_2, acidity and black smoke) for specific periods are given in Table 6.8.

Table 6.10 Summary of the Monthly Linear Regression Slopes for PM_{10} and Traffic Pollutants for each Site During 1994.

Site	**PM_{10} vs NO_x Regression Slope**	**Number of Valid Months**	**PM_{10} vs CO Regression Slope (*1000)**	**Number of Valid Months**
Belfast	0.185 ± 0.038	11	16.6 ± 0.31	7
Bexley	0.078 ± 0.022	3	13.9 ± 0.63	2
Birmingham	0.134 ± 0.029	12	16.9 ± 0.12	8
Birmingham East	0.098 ± 0.019	6	16.6 ± 0.45	4
Bristol	0.096 ± 0.029	11	17.0 ± 1.10	5
Cardiff	0.127 ± 0.046	5	11.6	1
Edinburgh	0.081 ± 0.012	5	14.9	1
Hull	0.100 ± 0.022	8	20.4 ± 0.96	4
Leeds	0.113 ± 0.042	7	16.1 ± 0.43	5
Leicester	0.103 ± 0.020	6	14.1 ± 0.34	4
Liverpool	0.119 ± 0.027	10	20.6 ± 0.51	5
London				
Bloomsbury	0.100 ± 0.024	10	22.8 ± 0.62	3
Newcastle	0.106 ± 0.026	12	18.4 ± 0.53	6
Southampton	0.093 ± 0.036	9	13.6 ± 0.61	9
All Data	0.110 ± 0.027		16.7 ± 0.31	
Traffic Emissions: UK 1980	0.062		13.4	
Traffic Emissions: UK 1990	0.060		11.6	
Traffic Emissions: Central London	0.073		12.0	

Note: Based on provisional data.

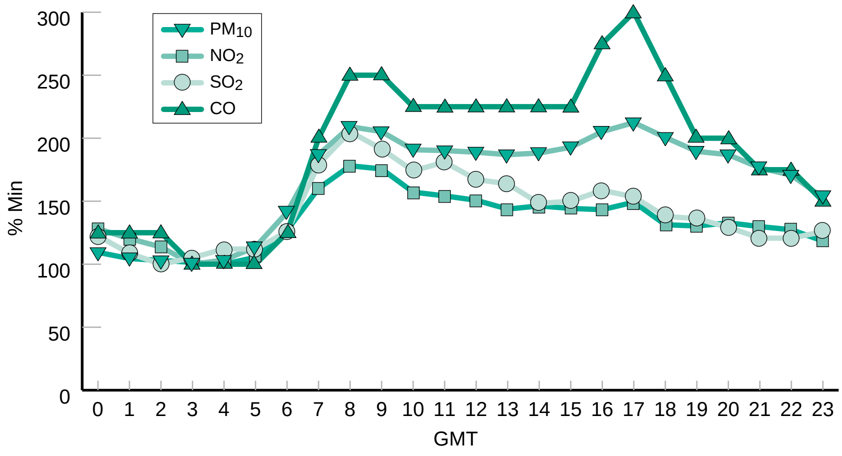
Coefficients greater than or equal to 0.75 have been highlighted.

These correlations show the proportion of the variation in PM_{10} concentrations that can be related to variations in other pollutants and not the proportion of the mean PM_{10} concentration that can be attributed to particular sources. However, correlation coefficients between PM_{10} and vehicle-derived and other pollutants provide some indication of the sources of PM_{10} at each site. For example, at Cardiff, the correlation between PM_{10} and NO_x or CO is relatively small suggesting that non-vehicle sources made a larger contribution to the PM_{10} concentrations at this site during 1992/93.

Hourly concentration data for PM_{10}, carbon monoxide and NO_x (=$NO+NO_2$) for each AUN site for 1994 were processed in calendar month subsets containing 720-744 hourly data points for 100% data capture. Linear regression analyses were performed and were found to be significant for most sites and months for both the combinations of PM_{10} and CO and PM_{10} and NO_x. Figures 6.20 and 6.21 present the slopes of the regression equations for each site and month, showing those regression equations which were well-defined with $R>0.5$, for $n<744$. Up to twelve regression slopes are plotted for each site and those with a well-defined regression equation are marked with an asterisk. For some sites during 1994, the PM_{10} vs NO_x regression slopes are well-defined for all months: Belfast, Bristol, Newcastle and Birmingham.

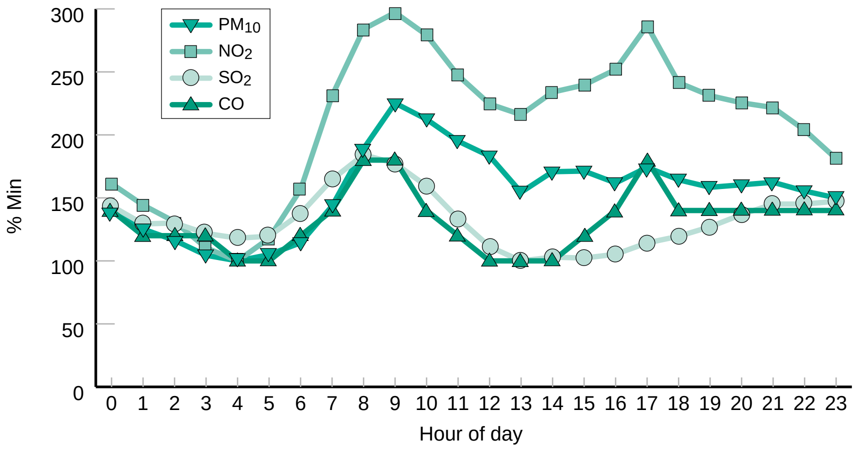
During the winter months, the correlations between PM_{10} and NO_x were highly significant at all sites. During the spring and summer months, the correlation became less significant at some, but not at all sites. Similar behaviour was seen in the correlations

Figure 6.22a **Bristol 1993 Diurnal Plot.**



Note: Values are plotted as a proportion of the minimum.

Figure 6.22b **Belfast 1993 Diurnal Plot.**



Note: Values are plotted as a proportion of the minimum.

between PM_{10} and carbon monoxide, which were found to be highly significant during the winter. However, almost all sites showed little evidence of correlation between PM_{10} and CO during the summertime.

Table 6.10 compares the linear regression slopes between PM_{10} vs CO and PM_{10} vs NO_x with the corresponding estimates of the respective ratios of the emissions. The level of agreement between the air quality data and the emission inventories is most encouraging.

6.5.2 Diurnal Variation of Particulate Matter

The measurements from the automatic monitoring stations allow the diurnal variation of PM_{10} and a number of other pollutants during the working week to be investigated as shown in Figure 6.22a and 6.22b for Bristol and Belfast. The pollutants are plotted relative to the minimum hourly value which typically occurs in the early hours of the morning. The pollutant levels all increase substantially during the early morning with a maximum concentration at about 08.00 hours. This feature is characteristic of traffic-related pollutants for which emissions peak in the morning travel-to-work time, or of pollutants which are depleted in the shallow night-time boundary layer

Table 6.11 Seasonal Variation in PM_{10} and Other Pollutants for the Pollution Year 1993/94.

Pollutant	**PM_{10} Ratio of summer to winter seasonal**		**CO Ratio of summer to winter seasonal**		**NO_2 Ratio of summer to winter seasonal**		**SO_2 Ratio of summer to winter seasonal**		**O_3 Ratio of summer to winter seasonal**	
Site	**Means**	**98th Percent.**	**Means**	**98th Percent.**	**Means**	**98th Percent.**	**Means**	**98th Percent.**	**Means**	**98th Percent.**
Belfast	0.84	0.75	0.63	0.34	0.80	0.94	0.48	0.46	1.29	1.06
Bristol	0.93	0.90	0.88	0.65	-	-	1.00	1.10	1.13	1.14
Birmingham (Central)	1.00	1.05	1.00	0.80	0.88	1.09	1.00	1.28	1.31	1.11
Cardiff	-	-	0.63	0.50	0.80	0.92	1.00	1.14	1.58	1.46
Edinburgh	1.05	0.91	0.86	0.65	0.96	1.08	0.70	0.77	1.25	1.00
Leeds	0.93	0.83	0.78	0.57	0.75	0.85	0.75	0.87	1.50	1.19
Liverpool	0.81	0.85	0.83	0.72	-	-	0.65	0.97	-	-
London (Bloomsbury)	1.00	0.99	0.83	0.75	0.92	1.08	0.69	0.58	1.57	1.41
Newcastle	-	-	0.88	0.71	0.97	1.02	0.88	0.74	-	-
Average (All Sites)	0.94	0.90	0.81	0.63	0.87	1.00	0.79	0.88	1.38	1.19

but remain at daytime concentrations aloft. The diurnal variation of the pollutants which are primarily derived from motor vehicle emissions show a pronounced second maximum as observed at the Bristol site for carbon monoxide and nitrogen dioxide. For PM_{10}, there is no discernible second maximum but rather a gradual decline throughout the rest of the day. A similar trend is observed at the other national sites. This is apparently consistent with the different emission and use patterns of light and heavy duty vehicles through the course of the day.

6.5.3 Seasonal Variation of Particulate Matter

Table 6.11 compares the ratios of the summer (April to September) to the winter (October to March) seasonal means for PM_{10}, CO, NO_2, SO_2 and O_3 and the corresponding ratios for the 98th percentile levels. The ratios for PM_{10} are close to one, apparently indicating little seasonal variation. This is in contrast to the behaviour of the primary pollutants such as CO or SO_2 which show larger winter concentrations or of that of O_3 which is a secondary pollutant with a distinct summer maximum. Closer examination of the daily average concentration of PM_{10} recorded in each month between 1992 and 1994, as shown in Figure 6.23, reveals a more complex behaviour. Generally, days of highest PM_{10} concentration occur in winter rather than in summer. It is clear from the ratios presented in Table 6.11 that PM_{10} has other sources compared to those pollutants, such as CO or NO_x, which are derived predominantly from motor vehicle emissions. This again confirms the role of other sources of PM_{10} such as secondary aerosol formation.

6.5.4 Behaviour of Particulate Matter in Episodes

Two specific types of air pollution episodes can be identified - the so-called “summertime” and “wintertime” smog episodes. Summertime air pollution episodes are associated with anticyclonic conditions, light winds, high temperatures and clear skies whereas wintertime smog episodes which also occur under anticyclonic conditions are accompanied by low or light winds, low temperatures and shallow mixing layer depths. In the fourth MAAPE report (MAAPE, 1995), clusters of pollutants were identified which could be used to characterize such episodes. The summertime episode was characterized by elevated concentrations of O_3 which are strongly anti-correlated with those of NO_2. Indeed, it is often the sum of O_3 and NO_2 which is used in analyses since this gives the total oxidant present in the atmosphere. The wintertime episodes were sub-divided into two classes:

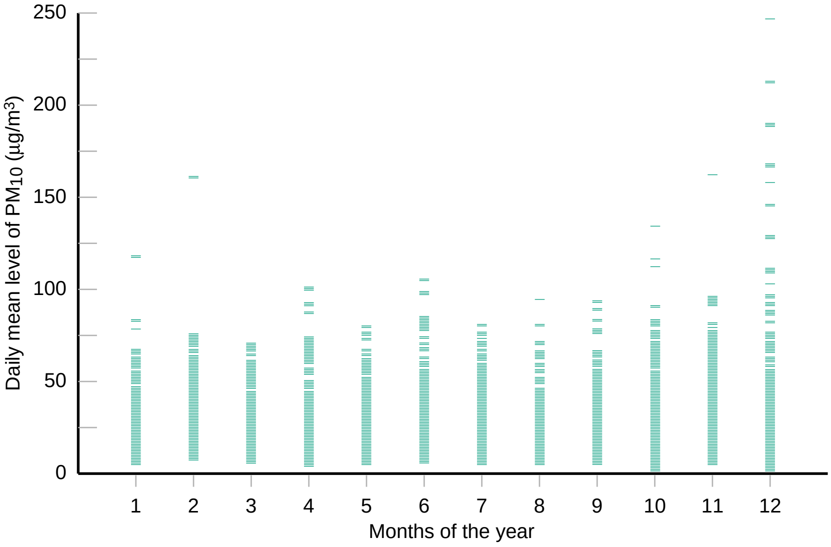
(a) the traditional wintertime smog episode in which SO_2, CO and PM_{10} were strongly correlated, with a less strong association to NO_2.

(b) those resulting primarily from motor vehicle emissions in which the cluster of CO, PM_{10} and NO_2 could be identified.

An example of a summertime episode is that observed at the London Bloomsbury site in June 1993. Figure 6.24 shows the simultaneous rise and fall of the daily-averaged levels of PM_{10} and five other pollutants during the episode. Analysis of this episode indicated a stronger correlation between PM_{10} and O_3 suggesting a significant secondary component to the PM_{10} fraction. A wintertime episode which occurred in Belfast and Birmingham during December 1994 is shown in Figure 6.25. In this episode, strong correlations can be seen between the hourly-averaged concentrations of PM_{10} and a number of the other pollutants. There are several other examples which could have been used to illustrate the same point. Other pollutants such as benzene, which arises predominantly from motor vehicle emissions, also show periods when a strong correlation exists with PM_{10}. The benzene and PM_{10} measurements made at the London Bloomsbury site for the period from 6 to 12th October 1994 are shown in Figure 6.26 and the scatter plot is given in Figure 6.27.

In the fourth MAAPE report (MAAPE, 1995), those periods in 1992 and 1993 when the concentrations of O_3 (≥ 90 ppb or 180 µg/m³) NO_2 (≥ 100 ppb or 191 µg/m³) and SO_2 (≥ 125 ppb or 357 µg/m³) were elevated have been analysed to identify correlations between pollutants. Correlations between pairs of pollutants were determined. When hourly average concentrations of O_3 were equal to or exceeded 90 ppb, the only strong correlations identified were

Figure 6.23 Daily Mean PM_{10} Concentrations from the AUN, 1992 - 1994.



Note: Based on ratified data.

Figure 6.24 Daily-Mean PM_{10} and other Pollutants; London; June 1993.

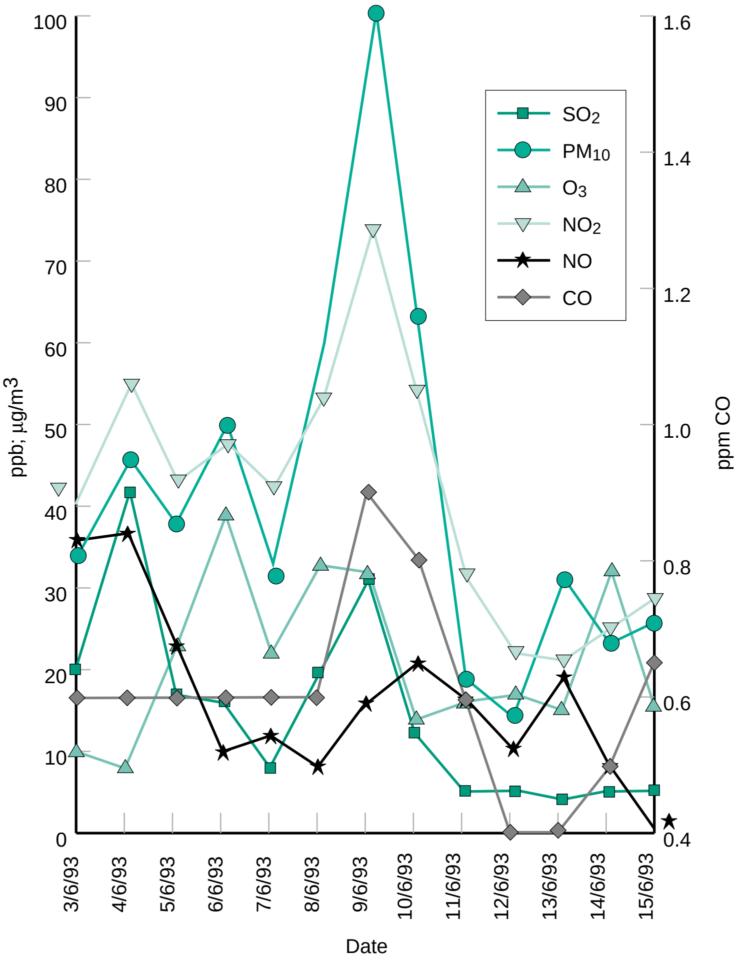


Figure 6.25a **Hourly-mean PM_{10} and Other Pollutants, Belfast, 21st - 23rd December 1994.**

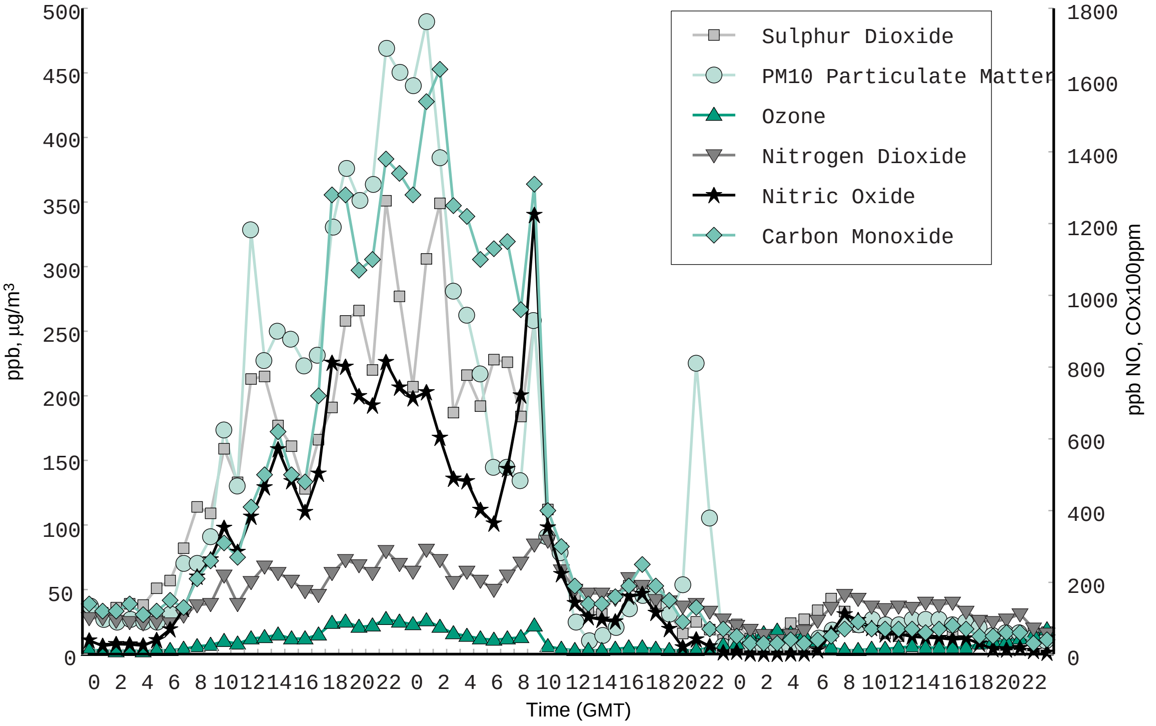


Figure 6.25b **Hourly-mean PM_{10} and Other Pollutants, Birmingham Centre, 21st - 23rd December 1994.**

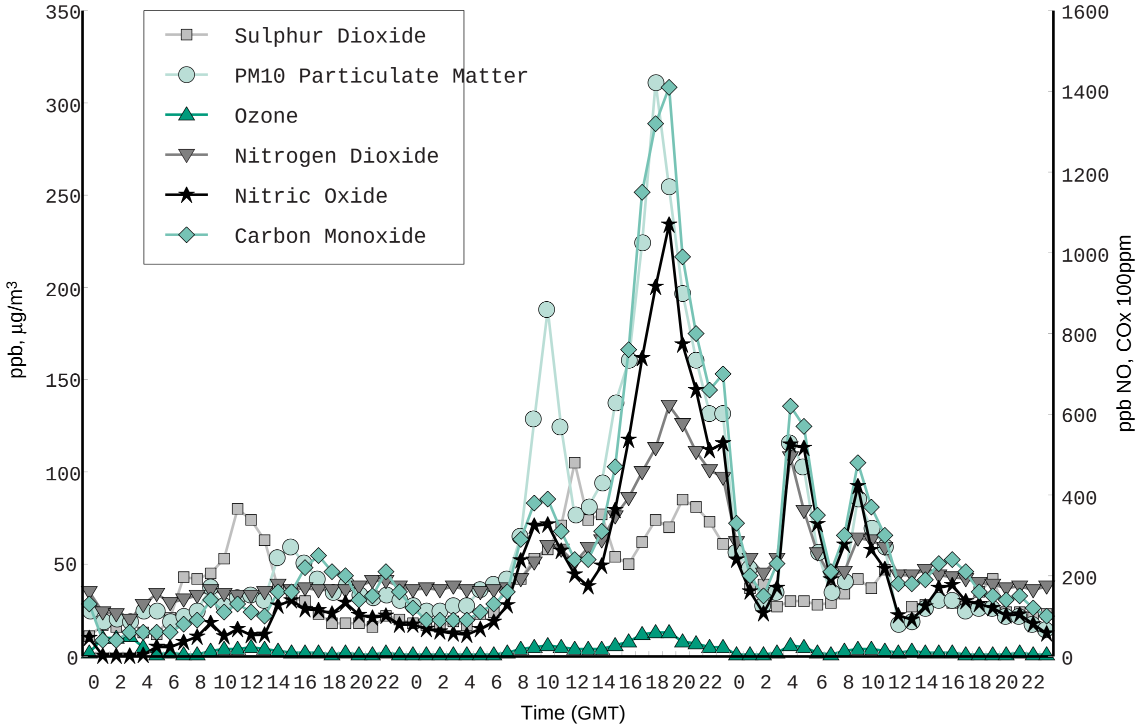


Figure 6.26 **Hourly-mean PM_{10} and Benzene, Bloomsbury 6 - 12 October 1994.**

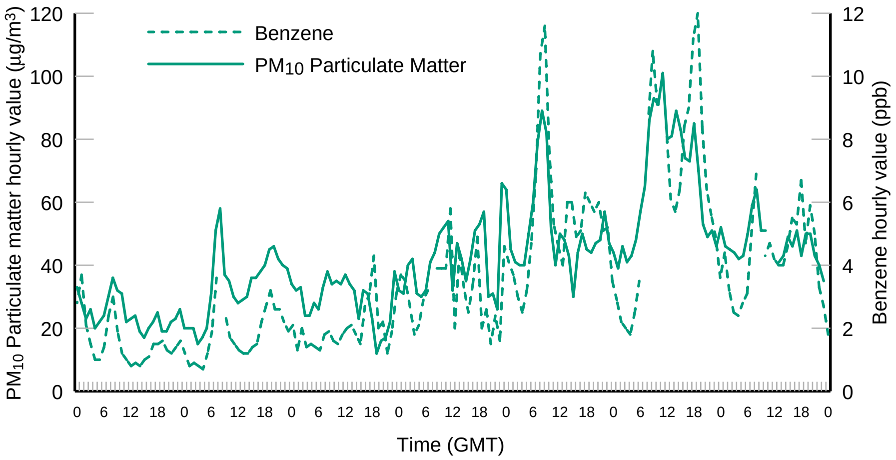
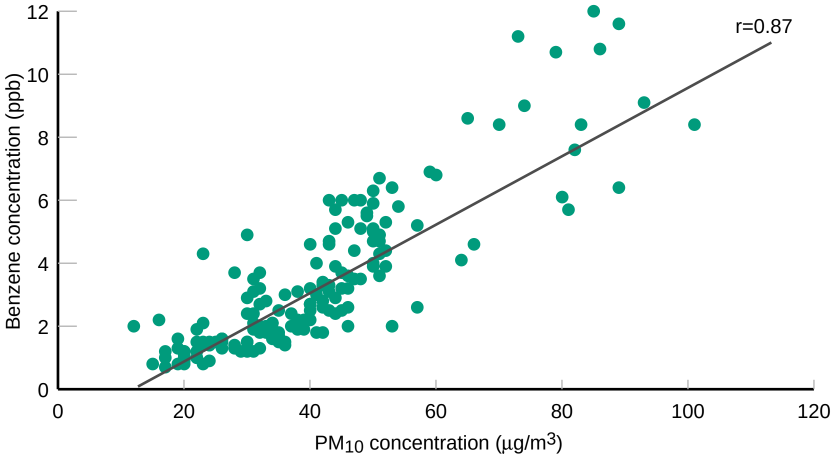


Figure 6.27 **Correlation of Hourly-mean PM_{10} and Benzene, Bloomsbury 6 -12 October 1994.**



between O_3 and NO_2 and O_3 and NO_x. The averaged concentrations of all the other pollutants were depressed except for PM_{10}, as shown in Table 6.12. For hourly concentrations of NO_2 equal to or greater than 100 ppb, the strongest correlations were with CO and PM_{10} and to a lesser extent, SO_2. There were strong correlations between SO_2 and all the other pollutants except for O_3 when hourly concentrations of SO_2 were equal to or greater than 125 ppb. It should be noted that most of these episodes of elevated concentrations of SO_2 occurred at the Belfast site. The mean concentrations of the pollutants observed during the periods when the concentrations of NO_2 or SO_2 were elevated are also given in Table 6.12. These mean levels are again compared to the mean concentrations determined from all the available measurements. The analysis indicates that elevated PM_{10} concentrations are associated with elevated levels of NO_2 or O_3. An association with elevated concentrations of SO_2 is also evident but this is heavily influenced by the measurements made at the Belfast site.

6.5.4.1 Particle Concentrations During the December 1991 Episode

In previous QUARG Reports, reference has been made to the December 1991 episode when unprecedented concentrations of NO_2 were reported in central London. Concentrations of many other pollutants also reached elevated levels and for the

Table 6.12 Analysis of Periods in 1992 and 1993 when Concentrations of $O_3 \geq 90$ ppb, $NO_2 \geq 100$ ppb or $SO_2 \geq 125$ ppb (MAAPE, 1995).

Analysis of Measurements for O_3 Concentrations ≥ 90 ppb

Pollutant	Mean when $O_3 \geq 90$ ppb	Number of such Measurements	Mean of all data
O_3 (ppb)	94	13	14
NO_2 (ppb)	13	13	26
NO_x (ppb)	14	13	64
CO (ppm)	0.5	13	0.7
PM_{10} ($\mu g/m^3$)	40	13	28
SO_2 (ppb)	5	13	10

Analysis of Measurements for NO_2 Concentrations ≥ 100 ppb

Pollutant	Mean when $NO_2 \geq 100$ ppb	Number of such Measurements	Mean of all data
O_3 (ppb)	9	52	14
NO_2 (ppb)	126	63	26
NO_x (ppb)	530	61	64
CO (ppm)	3.2	59	0.7
PM_{10} ($\mu g/m^3$)	127	49	28
SO_2 (ppb)	57	59	10

Analysis of Measurements for SO_2 Concentrations ≥ 125 ppb

Pollutant	Mean when $SO_2 \geq 125$ ppb	Number of such Measurements	Mean of all data
O_3 (ppb)	7	152	14
NO_2 (ppb)	58	148	26
NO_x (ppb)	367	148	64
CO (ppm)	6.0	155	0.7
PM_{10} ($\mu g/m^3$)	207	145	28
SO_2 (ppb)	172	155	10

majority, these have not been approached at any time since.

Typical daily average black smoke levels in central London sites during winter lie in the range 10-30 $\mu g/m^3$. During the December 1991 episode, however these concentrations rose to levels which were an order of magnitude higher, 150-200 $\mu g/m^3$. Daily average concentrations of black smoke for 11 London sites during December 1991 are shown in Table 6.13 (Anderson et al, 1995). It is interesting to note that the maximum values observed in 1991 are an order of magnitude lower than the corresponding maxima during the London smogs of the 1950s and 60s. This emphasises once again the different nature of the 1991 winter episode to previous episodes as discussed in the first QUARG report.

Unfortunately, automatic hourly measurements of PM_{10} had not commenced in London at the time of the December 1991 episode. It is interesting, however, to speculate what the corresponding PM_{10} concentrations would have been during the episode to resolve the relative importance of a range of causative factors and agents in bringing about the observed public health response.

The 11 black smoke monitoring sites operating in London showed daily average levels on the 12th December 1991 ranging from 7 to 228 $\mu g/m^3$. The average concentration of black smoke on that day was 113 $\mu g/m^3$ which is 83 $\mu g/m^3$ above the monthly mean of the 11 stations (30 $\mu g/m^3$). The black smoke to PM_{10} ratio is known to vary by season and by site, but based on simultaneous measurements of both made in

Table 6.13 Daily Black Smoke Concentrations (µg/m3) Recorded in London, December 1991.

Day	Acton 15	Camberwell 4	City 16	Croydon 15	Ealing 7	Enfield 14	Ilford 6	Islington 9	Kensington 13	Stepney 5	Westminster 17	Mean	Max
1													
2													
3	11	12	18	13	17	8	10	7	14	7	15	12	18
4	11	12	20	16	16	7	10	11	12	9	26	14	26
5	14	14	20	24	21	4	7	11	25	7	17	15	25
6	30	35	35	16	42	10	28	11	49	21	49	30	49
7	60	40	47	14	71	16	61	7	41	26	68	41	71
8	45	54	53	13	63	11	44	4	54	24	65	39	65
9	45	61	62	11	63	11	52	16	55	24	48	41	63
10	32	31	42	8	42	11	1	11	43	20	40	26	43
11	57	58	63	13	82	22	65	12	49	26	52	45	82
12	153	125	140	15	209	24	228	7	166	31	148	113	228
13	162	80	128	15	167	26	181	12	158	36	121	99	181
14	110	88	105	10	124	13	80	12	145	36	99	75	145
15	81	38	81	13	71	17	58	7	84	31	81	51	84
16	44	25	37	25	35	7	24	7	31	24	38	27	44
17	41	8	15	12	15	13	14	4	16	8	14	15	41
18	12	5	14	13	8	2		3	9	6	7	8	14
19	11	4	19	26	4		14	7	5	6	5	10	26
20	9	6	9	34	5		7	11	7	8		11	34
21	2	2	5	16	3		6	7	4	5		6	16
22	3	2	8	28	1		4	7	4			7	28
23	7	4	14	8	7		6	11	3		5	7	14
24	16	15	15	32	17		18	11	12		17	17	32
25	14	12	20	13	12		13	3	12		12	12	20
26	4	4	10	13	3	8	3	7	4		3	6	13
27	23	28	15	11	23	4	28	7	21		26	19	28
28	27	12		16	25	3	32	3	21			17	32
29	21	19		22	25	3	15	7	14			16	25
30	34	20		20	38	8	24	7	19			21	38
31													
Mean	39	29	40	17	43	11	38	8	38	19	43	30	
Max	162	125	140	34	209	26	228	16	166	36	160		

Table 6.14 Limit and Guide Values for Smoke and Sulphur Dioxide (in µg/m^3) Specified in EC Directive on Smoke and Sulphur Dioxide (80/779/EC).

(1) Limit Values

Reference Period	**Limit Values for**	
	Smoke	**Sulphur Dioxide**
Pollution Year (median of daily values)	68	120 if smoke ≤ 34 80 if smoke > 34
Pollution Year (98th percentile of daily values)	213	350 if smoke ≤ 128 250 if smoke > 128
Winter (median of daily values Oct-Mar)	111	180 if smoke ≤ 51 130 if smoke > 51

(2) Guide Values

Reference Period	**Guide Values for**	
	Smoke	**Sulphur Dioxide**
Year (arithmetic mean of daily values)	34-51	40-60
24 hours (daily mean values)	85-128	100-150

Note: Limit and Guide Values given for smoke are for the BS calibration as used in the UK. The limits stated in the EC Directive relate to the OECD method; the relationship between concentration determined using the OECD and BS calibration is: BS = 0.85 OECD.

1992, the best estimate of the mean PM_{10} increase across London during the episode is 110 µg/m³. On this basis, the increase in black smoke and PM_{10} could explain some of the increase in mortality and morbidity observed in London (Anderson et al, 1995).

6.6 EXCEEDENCES OF AIR QUALITY STANDARDS AND GUIDELINES

Air Quality guidelines and standards currently exist for particulate matter characterized as black smoke or total suspended particulate and PM_{10}. The EC Directive (80/779/EC) on Sulphur Dioxide and Suspended Particulate Matter gives separate guide and limit values for smoke and suspended particulate matter. As stated earlier, there is no simple relationship between black smoke and total suspended particulate and the United Kingdom has chosen to implement the Directive using black smoke measurements (Annex 1 of the Directive) (Table 6.14). The Directive also gives guide and limit values for sulphur dioxide but these are dependent on the associated concentration of smoke (Table 6.14). This linkage of the two pollutants arose from the observations and epidemiological studies of the London smog episodes. The limit and guide values for suspended particulate matter are currently used in the Department of Transport's Design Manual for Roads and Bridges (DOT, 1994).

Table 6.15 gives the number of exceedences of the EC Directive from the 1987/88 pollution year to the 1994/95 pollution year. In the pollution year 1993/94, there were no exceedences of the EC Directive. As part of the Directive, a number of derogation areas were established, principally where coal remained a significant fuel source and breaches of the Directive could possibly occur. Since 1993, such derogations no longer exist.

The World Health Organization has recommended air quality guidelines for particulate matter, which are linked to the concentration of sulphur dioxide. The current guideline values are summarised in Table 6.16

Table 6.15 Exceedences of the EC Directive for SO_2 and Suspended Particulate Matter.

Site	**Pollution Year/Criterion**							
	1987/88	**1988/89**	**1989/90**	**1990/91**	**1991/92**	**1992/93**	**1993/94 (a)**	**1994/95 (a)**
Crewe 17	Sm≥3cd	-	-	-	-	-	-	-
Mexborough 19	Sm≥3cd	-	-	-	-	-	-	-
Seaham 2	Sm/98, Sm≥3cd	-	-	-	-	-	-	-
Hetton-le-Hole 3	Sm/98, Sm≥3cd	Sm/98	Sm/98, Sm>3cd	-	-	-	-	-
Houghton-le-Spring 3	Sm/98, Sm≥3cd	-	-	-	-	-	-	-
Sunderland 8	Sm/98	-	-	-	-	-	-	-
Featherstone 1	Sm/98, Sm≥3cd	-	-	-	-	-	-	-
Washington 4	Sm≥3cd	-	-	-	-	-	-	-
New Ollerton 2	-	Sm≥3cd	-	-	-	-	-	-
Durham Sherburn 1	-	-	-	-	Sm/98	-	-	-
Grimethorpe 3	-	-	-	-	-	(b)	-	-
Belfast 11 (c)	-	-	-	Sm/98, Sm≥3cd	-	-	-	-
Belfast 12 (c)	-	-	-	Sm/98, Sm≥3cd	-	-	-	-
Belfast 39 (c)	Sm≥3cd	Sm/98, Sm≥3cd	-	-	-	-	-	-
Belfast 42 (c)	-	-	Comb/98	Comb/98 Comb≥3cd	Comb/98	-	-	-
Newry 3 (c)	-	-	Sm/98, Sm≥3cd	-	-	-	-	-

Criteria (1) Sm/98 - limit value for the 98th percentile of daily values in a year exceeded for black smoke.
(2) Sm≥3cd - at least one period of 3 or more consecutive days when daily values were above the 98th percentile limit value for black smoke.
(3) Comb/98 - both black smoke and SO_2 98th percentiles exceeded the combined limit values (i.e. 128 $\mu g/m^3$ BS or 150 $\mu g/m^3$ OECD for smoke and 250 $\mu g/m^3$ for SO_2).
(4) Comb≥3cd - at least one period of 3 or more consecutive days when daily values were above the 98th percentile limit values of both black smoke and sulphur dioxide.

Notes (a) There were no exceedences of the Directive in 1993/94 and 1994/95.
(b) The only exceedence in 1992/93 was at the Grimethorpe 3 site when the limit value for the 50th percentile of daily values in a year was exceeded for SO_2.
(c) Prior to 1993, a number of derogation areas existed, one of which covered the Belfast sites.

but are presently under revision. In America, the US EPA has established air quality standards for particulate matter. The primary standards which are set to protect human health are

- 24 hour mean concentration of 150 $\mu g/m^3$ PM_{10} which is not to be exceeded on more than 0.27% of occasions (1 in 365 days). This was previously set as 260 $\mu g/m^3$ TSP.

- arithmetic annual mean concentration of 50 $\mu g/m^3$ PM_{10} which was previously set as 150 $\mu g/m^3$ annual geometric mean TSP.

Table 6.16 WHO Guideline Values* for Combined Exposure to Sulphur Dioxide and Particulate Matter(a).

	Averaging Time	Sulphur Dioxide µg/m³	Reflectance Assessment: Black Smoke (b) µg/m³	Gravimetric Assessment	
				Total Suspended Particulate (TSP) (c) µg/m³	Thoracic Particles (TP) (d) µg/m³
Short Term	24 hours	125	125	120 (e)	70 (e)
Long Term	1 year	50	50	-	-

Notes

(a) No direct comparisons can be made between values for particulate matter since both health indicators and measurement methods differ. While numerically TSP/TP values are generally greater than those of black smoke, there is no consistent relationship between them, the ratio of one to the other varying widely from time to time and place to place, depending on the nature of the sources.

(b) Nominal µg/m³ units, assessed by reflectance. Application of the black smoke value is recommended only in areas where coal smoke from domestic fires is the dominant component of the particulate matter. It does not necessarily apply where diesel smoke is an important contributor.

(c) TSP: measurement by high volume sampler, without any size selection.

(d) TP: equivalent values as for sampler with ISO-TP characteristics (having 50% cut-off point at 10 µm); estimated from TSP values using site specific TSP/ISO-TP ratios.

(e) Values to be regarded as tentative as they are based on a single study which also involved sulphur dioxide exposure.

* currently under review.

Secondary standards have been established to protect the environment, to increase amenity, etc. These were originally different from the primary standards but have now been set to the same values as for the primary standards.

The Expert Panel on Air Quality Standards has recommended air quality standards for a number of atmospheric pollutants in the United Kingdom, including PM_{10}. The air quality standard recommended by EPAQS (1995) for PM_{10} is 50 µg/m³ as a 24-hour rolling average. Table 6.17 gives the number of exceedences of the EPAQS recommendation as well as those of a number of threshold levels, corresponding to daily mean concentrations of 50 µg/m³, 75 µg/m³, 100 µg/m³ and 150 µg/m³, which have been determined at each of the sites in the national automatic monitoring network for the years 1992 to 1994. Whilst it can be seen that there are a significant number of days at all sites for which the 50 µg/m³ level (both the EPAQS recommendation and the daily concentration) is exceeded, it is clear that there are progressively fewer exceedences of the higher thresholds with only a limited number of exceedences of the 150 µg/m³ threshold. More than one exceedence of the 150 µg/m³ daily level has occurred only at the Belfast site during this period. A further point to note from Table 6.17 is that the number of exceedences of the EPAQS recommended air quality standard for PM_{10} as a 24-hour rolling average is about two times greater than the number of exceedences which would have occured if the standard were expressed as a daily mean concentration of 50 µg/m³. Figure 6.23 shows the mean daily concentration of PM_{10} recorded at all the operational sites plotted for each month for the period from 1992 to 1994. It is evident from this figure that the highest concentrations of PM_{10} and therefore the greatest number of exceedences have tended to occur in the winter months when the dispersion of atmospheric pollution is poorer.

6.7 SPATIAL DISTRIBUTION OF PARTICULATE MATTER

6.7.1 *Across an Urban Area*

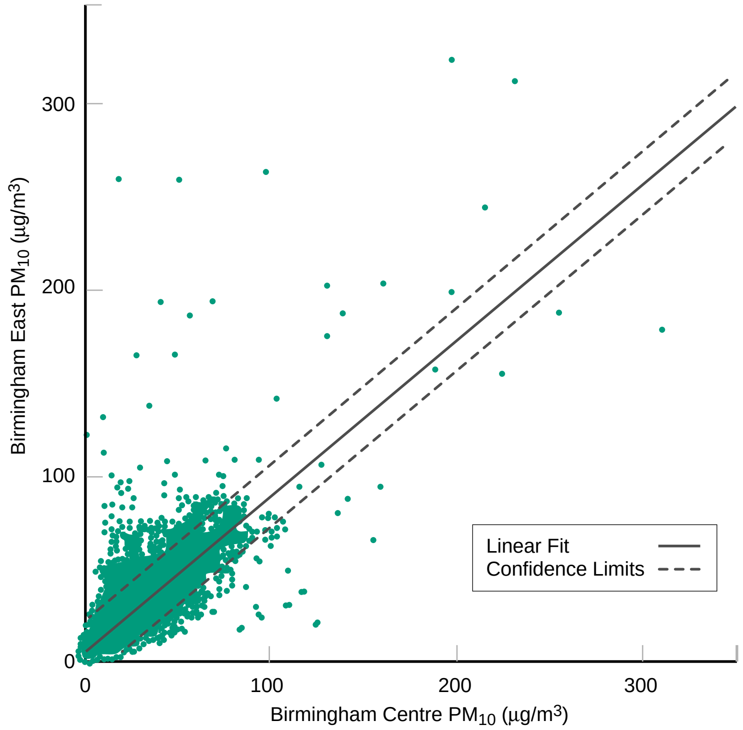
There is an extensive database of black smoke measurements for a range of industrial, residential and commercial site types in urban areas. Although these

Table 6.17 Exceedences Recorded between 1992 and 1994 for Various Threshold Values for Daily Average Levels of PM_{10}.

Site	Site First Operational	Year	Number of Days When Daily Mean PM_{10} Levels Exceeded				24 Hour Mean ≥50 µg/m³ EPAQS Count		Maximum Daily Mean PM_{10} Level µg/m³
			50 µg/m³	70 µg/m³	100 µg/m³	150 µg/m³		Days	
London (Bloomsbury)	Jan 1992	1992	27	4	0	0	628	43	94
		1993	31	10	0	0	788	57	100
		1994	17	3	0	0	485	39	93
Belfast	Mar 1992	1992	23	12	5	3	552	40	248
		1993	45	13	3	0	1075	80	120
		1994	17	6	3	2	433	32	191
Birmingham (Central)	Mar 1992	1992	21	6	1	0	526	37	131
		1993	25	5	1	0	568	39	102
		1994	15	3	1	0	366	23	113
Newcastle	Mar 1992	1992	21	3	0	0	487	38	72
		1993	14	4	0	0	430	32	79
		1994	23	1	0	0	481	39	77
Cardiff	May 1992	1993	21	3	0	0	492	40	89
		1994	55	13	0	0	1319	91	96
Edinburgh	Oct 1992	1993	2	0	0	0	39	4	66
		1994	1	0	0	0	30	3	62
Bristol	Jan 1993	1993	27	4	0	0	701	52	81
		1994	16	3	0	0	370	30	83
Leeds	Jan 1993	1993	23	4	0	0	594	40	96
		1994	24	7	1	0	549	44	114
Liverpool	Apr 1993	1993	22	6	0	0	449	28	163
		1994	19	5	0	0	471	34	84
Birmingham (East)	Dec 1993	1994	10	2	1	0	234	19	106
Hull	Jan 1994	1994	16	3	0	0	373	30	85
Leicester	Jan 1994	1994	5	0	0	0	178	17	65
Southampton	Jan 1994	1994	7	0	0	0	147	16	63

Note: Entries are only given for those sites which were operational for more than 9 months in a given year.

Figure 6.28 Hourly Concentrations of PM_{10} at Two Sites in Birmingham: Comparison of Sites for 1994.



data could be used to infer spatial distributions of particulate matter (as black smoke), the discussion on spatial distributions in this review will be limited to those of PM_{10}.

One of the more interesting features of the PM_{10} measurements made at the two sites in Birmingham is the very close correspondence between the concentrations observed. The data given in Table 6.1 for the measurements made in 1994 show the striking similarity not only of the annual mean levels but also in the 98th percentile and peak values. This indicates at least a degree of uniformity in urban concentrations at similar sites. Figures 6.8c and Figure 6.8d show the hourly measurements made at the two Birmingham sites between January 1994 and March 1995 (PM_{10} data for 1995 is provisional). Apart from the peak at the Birmingham East site in May 1994, the PM_{10} concentrations track together and this is further shown in the regression plot in Figure 6.28. A regression analysis indicates that the Birmingham East PM_{10} levels are about 84% of those measured at Birmingham Centre.

The same conclusion was drawn from the PM_{10} measurements made at three sites in the Bristol area. The sites consisted of the national monitoring station in the centre of Bristol, a location in the Avonmouth industrial area about 9 km from the national site and a suburban site at Shirehampton about 1 km from the Avonmouth site. The annual mean concentrations for the 12 month period to March 1995 were respectively 23, 23 and 20 µg/m^3 at the three sites. The uniformity across this urban area can also be seen in the daily average results, which are shown for June 1994 and January 1995 in Figures 6.29a and 6.29b. The concentrations follow each other very closely from day to day.

These limited results show little variation in average PM_{10} concentrations across urban areas and are consistent with the uniformity in the annual mean levels observed at the other urban background sites across the UK. A tentative conclusion to draw from these measurements is that one monitoring station can be representative of a particular site type in a given urban area.

Figure 6.29a Daily-mean PM_{10} Concentrations from Sites in the Bristol Area, June 1994.

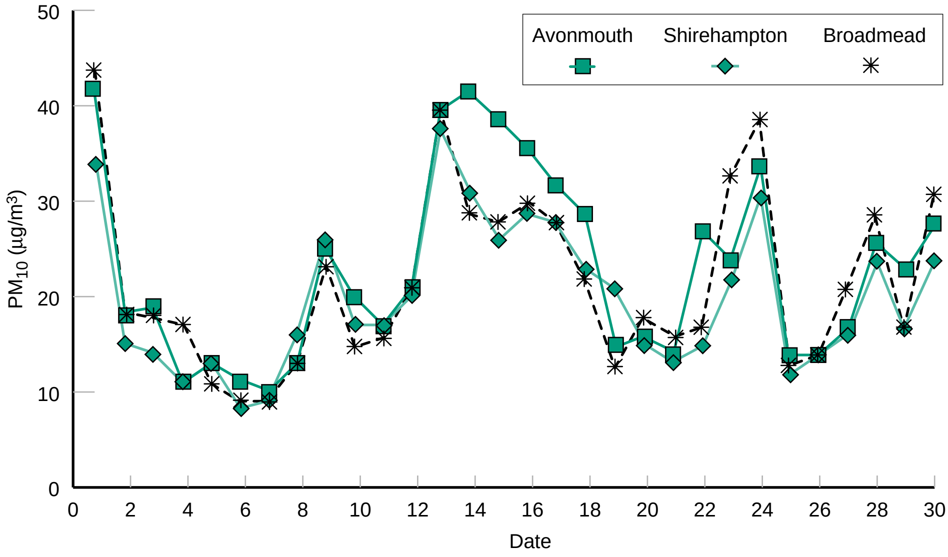
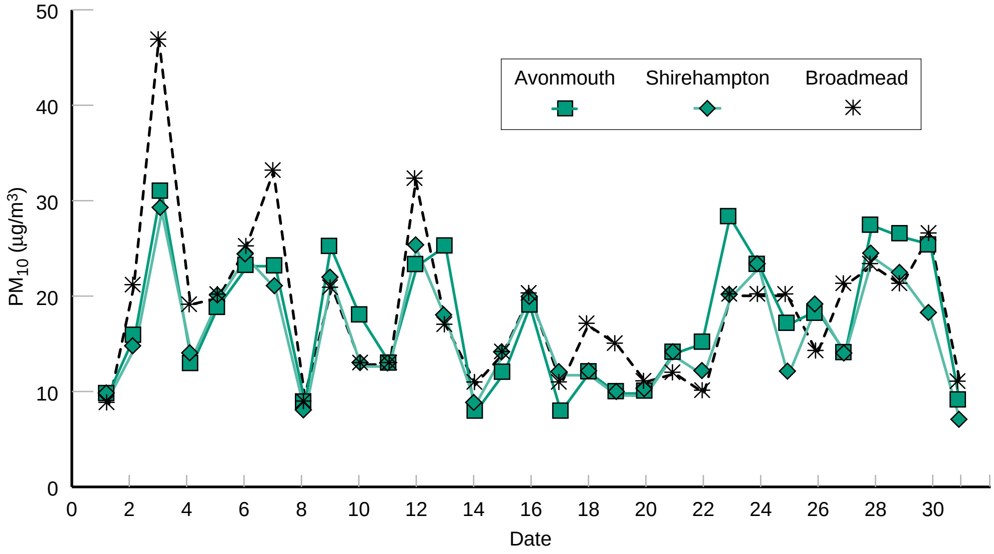


Figure 6.29b Daily-mean PM_{10} Concentrations from Sites in the Bristol Area, January 1995.

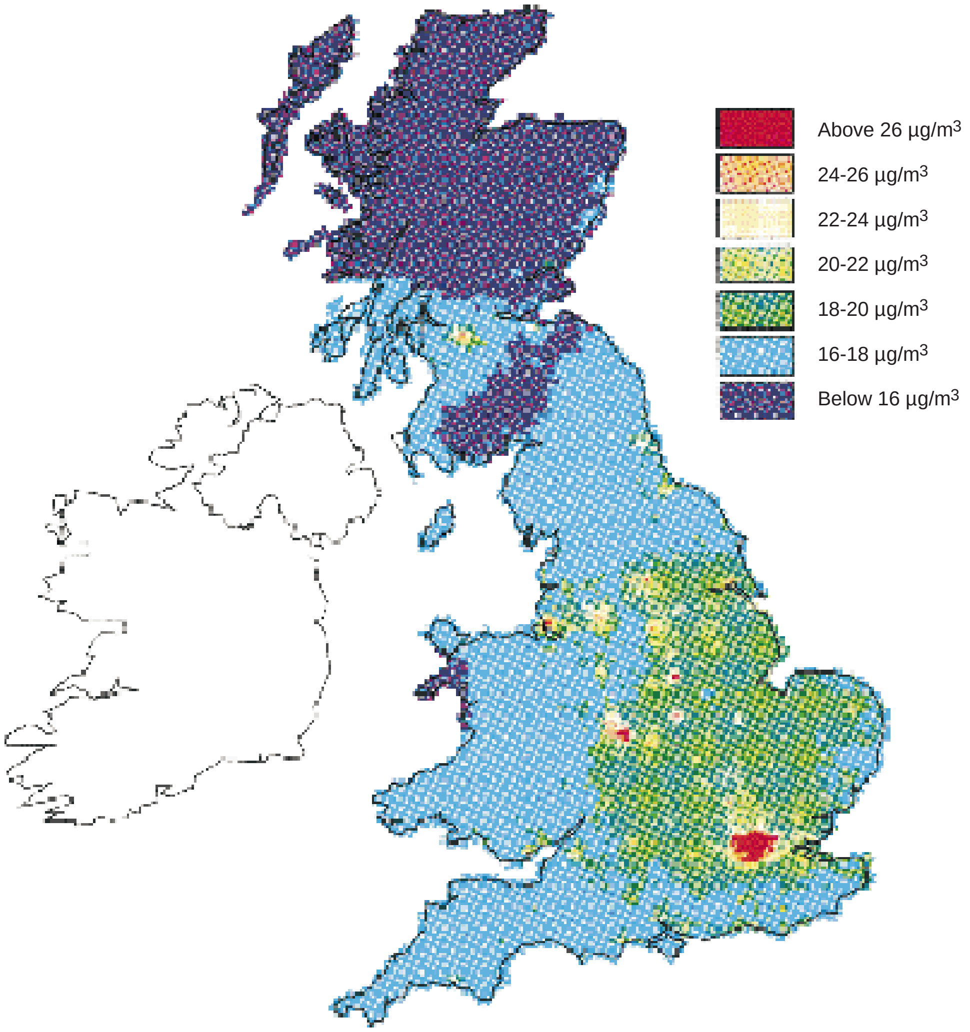


6.7.2 Across the United Kingdom

The spatial distribution of PM_{10} is of interest since it allows the annual exposure of different areas of the country to be assessed. The current measurements of PM_{10} have only been made at a limited number of sites across the United Kingdom and these do not allow the spatial distribution of PM_{10} across the whole country to be calculated reliably.

Whilst the smoke and sulphur dioxide network does provide a greater coverage of the UK, these measurements can only be used to infer the spatial distribution of PM_{10} providing the relationship between PM_{10} and black smoke has been established. Measurements have been undertaken to compare the levels of PM_{10} and of black smoke recorded at co-located or close sites as discussed in section 6.3.6. The analysis indicated that the relationships (between PM_{10} and black smoke) are very site specific. Further work is being undertaken to refine these observations.

Figure 6.30 Estimated Spatial Variation in Annual Mean PM_{10} Concentration Across the United Kingdom, 1991.



In the absence of direct data, the spatial distribution of PM_{10} has been inferred from the relationships between PM_{10} and other pollutants which have been measured on a larger spatial scale (Stedman, 1995). Two national NO_2 diffusion tube surveys (in 1986 and 1991) have been undertaken to derive monthly and annual levels of NO_2. The NO_2 measurements made in the 1991 survey were then mapped onto 5 km by 5 km grids covering the United Kingdom using population and land use statistics. These NO_2 maps were then used to generate firstly maps of NO_x and thence maps of PM_{10}. The co-located measurements of PM_{10} and NO_x made at the London Bloomsbury monitoring station were analysed to give a relationship between NO_x and PM_{10}. The regression analysis of the hourly PM_{10} and NO_x data for the two year period from the start of 1992 to the end of 1993 led to the relationship

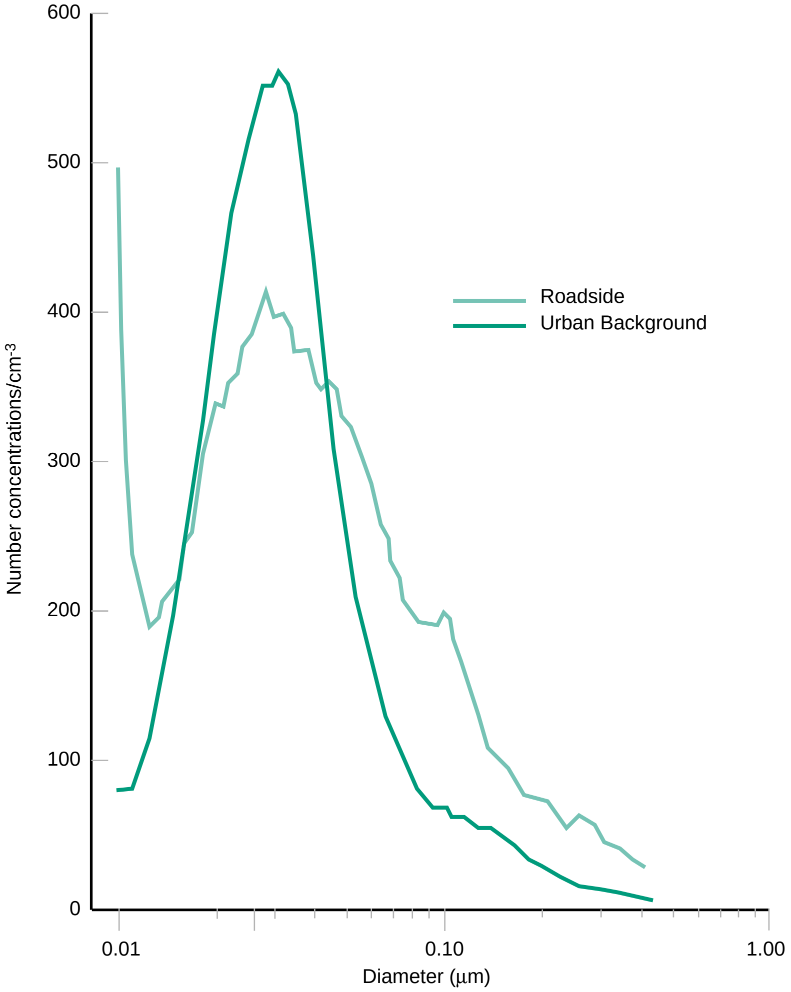
$$PM_{10} \text{ (in } \mu g/m^3) = 0.18\, NO_x \text{ (in ppb)} + 15.4$$

with a regression coefficient r^2 equal to 0.35. The annual mean concentrations of NO_2 and NO_x in 1993 determined at the automatic monitoring sites were analysed to give the relationship between NO_x and NO_2 in urban areas as $NO_x = 2.5\ NO_2$ ($r^2 = 0.5$). The expression for the relationship between NO_x and NO_2 in rural areas was derived from the ratio of the annual mean concentrations of NO_x and NO_2 recorded at the Lullington Heath site in 1993.

Figure 6.30 shows the map of estimated annual mean PM_{10} concentration (for 1991) derived in this manner for the United Kingdom (Stedman, 1995). It can be seen that the highest concentrations of PM_{10} are likely to be found in the south-east of England with annual mean levels above 26 µg/m³. The concentrations of PM_{10} may fall radially outwards from London. Major conurbations such as Birmingham, Manchester, Liverpool and Glasgow can be identified on these maps.

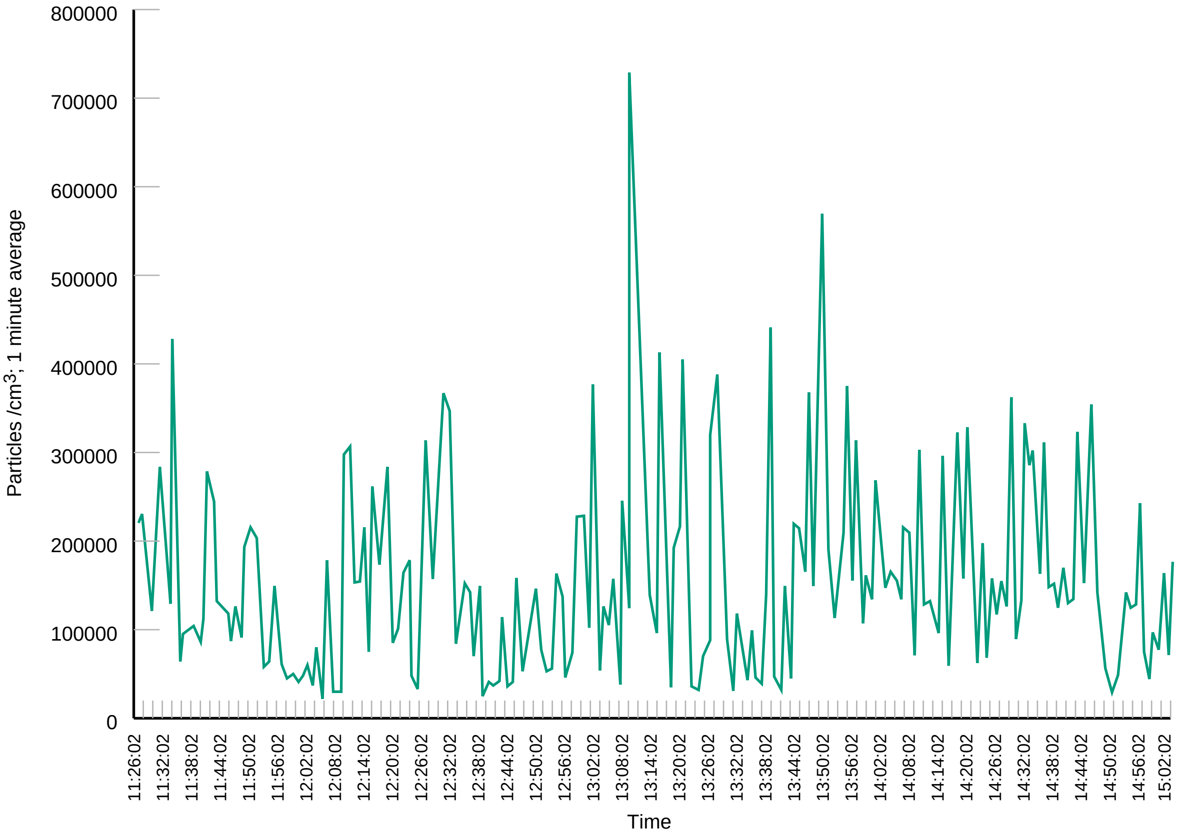
These maps, derived from maps of NO_x, can only take account of the likely variation in the vehicle-derived component of PM_{10}. As discussed above, there are other sources of particulate matter in the atmosphere, especially significant, when mean levels rather than episodes of elevated concentrations are considered. In these maps, other sources are taken account of by the 15.4 µg/m³ constant term. In future work, the variation of PM_{10} from other sources will be considered and the relationship derived between NO_x

Figure 6.31 A Comparison of Two Mean Particle Size Distributions, by Number.



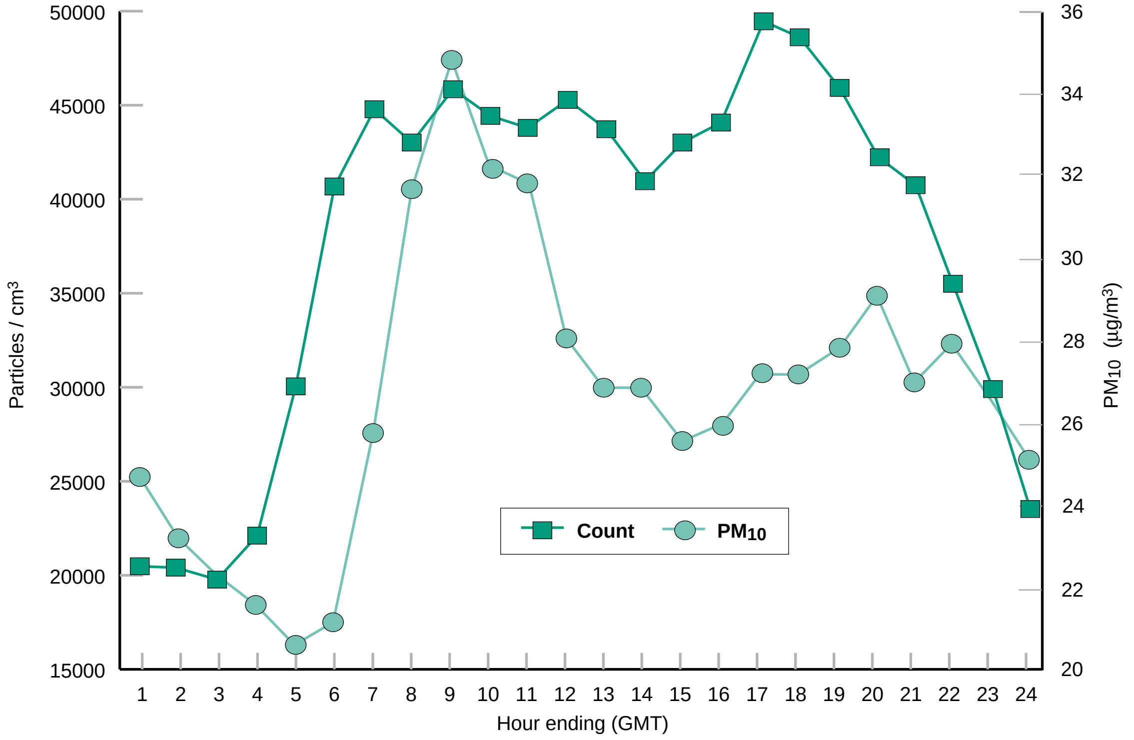
Source: Collins, Jones and Harrison, 1995.

Figure 6.32 Time Series of Particle Count Measurements Near a Busy Road in Birmingham.



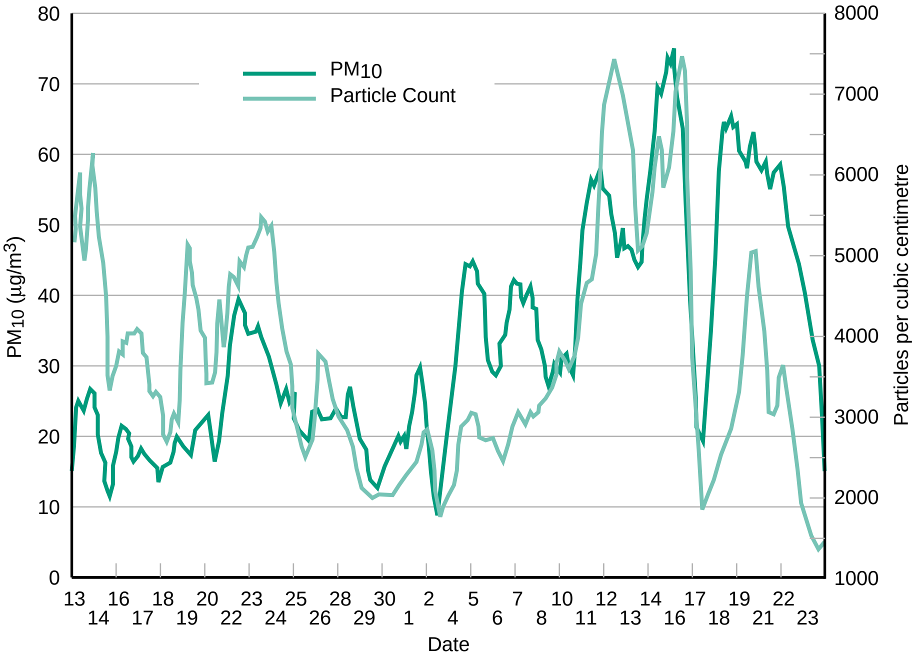
Source: Jones and Harrison, 1995.

Figure 6.33 Hourly-mean Diurnal Particle Count and PM_{10} Mass, Central Birmingham.



Source: Jones and Harrison, 1995.

Figure 6.34 24-Hour Rolling Mean PM$_{10}$ and Particle Count from a Site in Birmingham.



Source: Jones and Harrison, 1995.

and PM$_{10}$ will be refined using the larger amount of observational data now available.

6.8 ULTRAFINE PARTICLES AND PARTICLE NUMBER COUNTS IN URBAN AIR

The discussion thus far has concentrated solely on the mass of particulate matter measured at the different monitoring sites. There is a view that it is the total number of particles which is of concern rather than the total mass. There have been a number of studies in which the total number of particles as well as the total mass of the particulate matter have been determined.

As indicated in Chapter 2, there are abundant small particles in the atmosphere which contribute substantially to the total particle number count, but represent very little of the total mass concentration because of their tiny volume, and hence mass. These particles are termed ultrafine particles (generally defined as particles less than 50 nm in diameter). A size distribution (Figure 6.31) of particles sampled in the air of Birmingham and expressed in terms of particle number shows that the large majority of particles are smaller than 50 nm, and almost all are below 100 nm diameter. Thus, measures of particle number count, which may be made continuously with a condensation nucleus counter, are a good measure of the ultrafine particle loading.

Especially when close to sources of particle emissions, very large numbers of particles can be counted in urban air. Figure 6.32 shows a time series of particle count measurements taken 3 metres from the busy A38 Bristol Road in Birmingham as part of the DoE Air Quality Research Programme. The count varies rapidly between about 10^3 and 10^6/cm^3 with an average count of around 180,000/cm^3. A count made under similar weather conditions at a background site a few hundred metres away revealed a mean particle count of 27,000/cm^3. Thus particle numbers reduced about six-fold between the roadside site and the background due to dilution with cleaner air and particle coagulation processes which reduce the number count. Comparative measurements of PM$_{10}$ for the same sites indicate that the roadside site has PM$_{10}$ concentrations about 80% greater than the background site. This demonstrates clearly the very large impacts of freshly emitted particles upon the number count at the roadside site. These particles contribute relatively little to PM$_{10}$ mass because of their very small volume. These particle number concentrations may be compared with air over the North Atlantic Ocean, which in the absence of recent pollutant inputs shows typical particle number counts of around 200/cm³.

Measurements of particle count have also been made in central Birmingham at a background site adjacent to the PM_{10} measurements of the Birmingham (Central) Automatic Urban Network site. The majority of particle count data at this site were below 100,000 particles/cm³, although there were occasional excursions above this number, which was the upper limit of the instrument used for particle counting. Figure 6.33 shows moving average PM_{10} and particle count data through one 24 hour period. In general, the two measures of particle abundance are reasonably well related. The variation of particle number count and PM_{10} concentration over a five week sampling period is shown in Figure 6.34. The two exhibit roughly comparable patterns, although the number count starts to rise earlier in the morning than the PM_{10} concentration and does not fall in the afternoon in the way that PM_{10} does at this site. If 24 hour particle count data are correlated with PM_{10} over the same 24 hour intervals, the data show an approximately linear relationship with a correlation coefficient of 0.59.

Measurements made in London by Waller (1976) using electron microscopy revealed concentrations of the order of 10^4/cm³ at background sites, 3-5 x 10^4/cm³ in street samples and up to 16 x 10^4/cm³ in samples taken in tunnels and urban fogs. These measurements suggest that particle number densities have changed little since the 1960s although mass concentrations are expected to have diminished appreciably.

6.9 KEY POINTS

- *There has been a substantial decline in the concentration of particulate matter (as black smoke) over the past 40 years in both urban and rural locations across the United Kingdom. These measurements continue to provide a valuable source of information on the concentrations of particulate matter.*

- *With the introduction of automatic instruments, a sophisticated national urban monitoring network now exists to measure PM_{10}. The measurements have been made mainly in urban background locations and there is now a need to extend the measurement of PM_{10} to other site types.*

- *The annual mean concentration of PM_{10} at the urban background sites in the national Automatic Urban Monitoring Network lie between approximately 20 to 34 µg/m³. Although the annual mean concentrations appear relatively uniform across the United Kingdom, there is a substantial variation from day-to-day, from site-to-site, and from season-to-season.*

- *Analysis of the measurements of PM_{10} with those of other pollutants indicate that strong correlations exist between PM_{10} and CO and also between PM_{10} and NO_x at some locations. Such relationships can be used to infer the concentration of PM_{10} in the absence of direct measurements and for source apportionment.*

- *Attention is increasingly being focussed on the $PM_{2.5}$ size fraction. There are currently very few measurements of $PM_{2.5}$ concentrations in the United Kingdom. Measurements made at Birmingham indicate that the $PM_{2.5}$ size fraction can represent between 30 to 100% of the PM_{10} concentration, the proportion being dependent on the meteorological conditions.*

- *In general, there have been a few or no exceedences of a fixed 24-hour mean PM_{10} concentration of 100 µg/m³ at the sites in the national Automatic Urban Monitoring Network between 1992 and 1994, the exception being the Belfast site where 11 exceedences were observed. On the other hand, there have been widespread exceedences of a daily mean level of 50 µg/m³ at all sites in the network during this period.*

- *The EPAQS recommended standard of 50 µg/m³, 24-hour rolling mean, is exceeded more frequently than the same concentration measured over fixed 24-hour daily periods. Over the period 1992-1994 there were approximately double the number of exceedences of the 50 µg/m³ rolling mean, than of the same concentration expressed as a fixed daily mean.*

- *The number concentration of particles in urban air fluctuates widely, but normally lies between* 10^3 *and* 10^6 *per cubic centimetre. This reflects mainly the ultrafine particles which are very numerous but contribute little to* PM_{10} *mass.*

- *When averaged over 24 hour periods, particle number concentration is correlated with the* PM_{10} *mass and within a 24 hour period shows a similar diurnal variation.*

- *Particle number concentration is highly elevated close to a busy road, by a factor far greater than the elevation in* PM_{10} *mass.*

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7 The Chemical Composition of Airborne Particles in the UK Urban Atmosphere

7.1 INTRODUCTION

There have been numerous studies of some aspect of atmospheric particle chemistry undertaken on aerosol collected in the UK atmosphere. In this Chapter we seek to review that information and provide an estimate of "typical" UK airborne particle composition. Clearly, composition is variable in both time and space, and since no study has sought to characterise either kind of variation for more than one or two individual components, this point will not be addressed in detail.

The composition of atmospheric particles is influenced by a balance between sources, chemical transformations in the atmosphere, long-range transport effects and removal processes. Particles with a relatively long atmospheric lifetime and no significant localised sources (eg sulphate in fine particles) show quite high spatial uniformity on scales of tens, and possibly hundreds of kilometres. On the other hand, particles with short residence times and/or localised sources (eg quarry dust) show strong spatial concentration gradients. Thus no generalised statements on the degree of uniformity of atmospheric particles are possible. Undoubtedly there are substantial temporal and spatial variabilities in atmospheric particle loadings, and appreciable spatial variations in mean composition. Nonetheless, there are common chemical components which appear at relatively similar concentrations throughout the developed world (Sturges et al, 1989), and within the UK, airborne particle concentrations and composition are not expected to vary greatly from one location to another of the same type (eg urban) elsewhere in the country. There will, however, be local elevations in concentrations of some components, eg marine aerosol at coastal locations.

There are two main sources of information on aerosol composition in the UK atmosphere. Extensive national surveys have been carried out for individual components, chiefly metals and toxic organic compounds. As these studies have only investigated specific trace components of particulate matter, to obtain information on the bulk components use must be made of *ad-hoc* studies carried out by various research groups. This can lead to difficulties in comparing and combining the results obtained by different researchers as different sampling and analytical protocols were used.

A simple comparison of the raw published data from *ad hoc* studies is limited by the following difficulties:

1) There is no overall national strategy behind the selection of sampling sites. The majority of sites for which comprehensive studies have been made are not truly representative of the urban areas in which most people live.

2) There is no common standard for sampler design, so the fraction of particulate matter analyzed in different studies will often contain different particle size groups. It will be shown later that the composition of particles is highly dependent on their size.

3) There are large differences between analytical methods, and in the choice of species analysed.

4) The reported data cover an appreciable time interval and temporal changes in mean concentrations will have occurred over this time.

An additional source of data is from the two national particulate matter monitoring networks: the long-running and extensive National Survey of Air Pollution for black smoke, and the continuous PM_{10} instruments in the Automated Urban Network.

7.11 The Comparability of Data from Size Selective Samples

A frequently quoted distinction between size fractions is that of "fine" particles, aerodynamic diameter < 2.5 µm, and "coarse" particles, 2.5 to 10, or 15 µm. The 15 µm upper limit corresponds to the UK definition for "smoke"; 10 µm to the definition given earlier for PM_{10}. The "fine" fraction can be considered to be "respirable" and includes the "accumulation mode" and is thus the fraction of greatest interest (QUARG, 1993). The "coarse" fraction is largely "inhalable", but clearly includes a substantial fraction which are neither "thoracic" nor "respirable". (See Chapter 3 for definitions). The size fraction in which a species is predominantly found can tell a lot about the source of a species; if it is mostly found in the fine fraction it will probably be anthopogenic in origin. Natural dusts including marine aerosol are in most cases predominantly coarse.

Size selective samplers come in a variety of types with different size ranges employed. The two way division into "coarse" and "fine" is used in the so-called *dichotomous sampler* and has been employed in a study of urban air in Leeds by Clarke et al (1984). Size selection in this sampler is carried out using a virtual impactor, a device unlike the more usual cascade impactor. Because of its direct applicability to health effects studies, the dichotomous sampler is becoming increasingly popular, especially in the US where aerosol sampling has been far more widespread than in the UK. Most of the few UK studies which have taken size-resolved samples have used the cascade impactor which provides samples in several size ranges typically ranging from <0.5 µm to >12 µm. In most other studies of atmospheric particles no size discrimination is employed, making the data obtained less useful for evaluation of health effects. Obviously data from different size ranges are not directly comparable.

When different samplers which nominally capture the same size range are compared they will still not always agree. Studies comparing the High-Volume Sampler with the dichotomous sampler have shown that the Hi-Vol gives higher concentrations of total mass and of some ionic species, especially sulphate (Clarke et al, 1984 and Trijonis, 1983). This may be due, at least in part, to the formation of artefacts on the filter media: gaseous species in the incoming air react with some filter media and with collected particles to produce additional solid matter. Best known is the conversion of sulphur dioxide to sulphate on alkaline glass fibre media.

Even where size selection is used it has been found that the effects of high relative humidity can produce inconsistent results. Particles, especially those with a high sulphate content, will grow when exposed to high relative humidity thus changing their size distribution, a phenomenon investigated in detail by Koutrakis et al (1989). A US study by Keeler et al (1988) investigated the effect this has on dichotomous samplers and found that under extreme conditions 50% of the material usually found in the fine fraction will appear with the coarse. Given that night-time humidities are higher than daytime, and that most public exposure occurs indoors under conditions of low relative humidity, it seems likely that the "fine" fraction will frequently be underestimated by outdoor sampling. During a sampling campaign in Leeds by Clarke et al (1984) it was found that under conditions of high humidity their filters would clog up rapidly so the air was later pre-heated to avoid this problem. Such pre-heating will have altered the size distribution of their samples during the campaign. Pre-heating is also used on the TEOM continuous PM_{10} monitor (Patashnick and Rupprecht, 1991). Conventional methods using Hi-vols and dichotomous samplers do not employ pre-heating, rather the filters are conditioned to standard relative humidity before weighing. This has clear implications for the behaviour of both water content and the collection of volatile components leading to differences in gravimetric concentration. In this case size-distribution will not be affected because the heating is applied after the selective inlet.

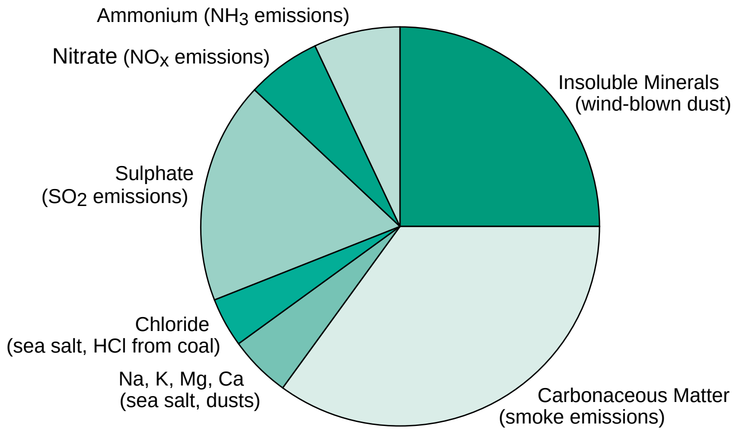
All these inconsistencies must be borne in mind when the results of the following sampling campaigns are discussed.

7.2 COMPOSITION OF AIRBORNE PARTICLES

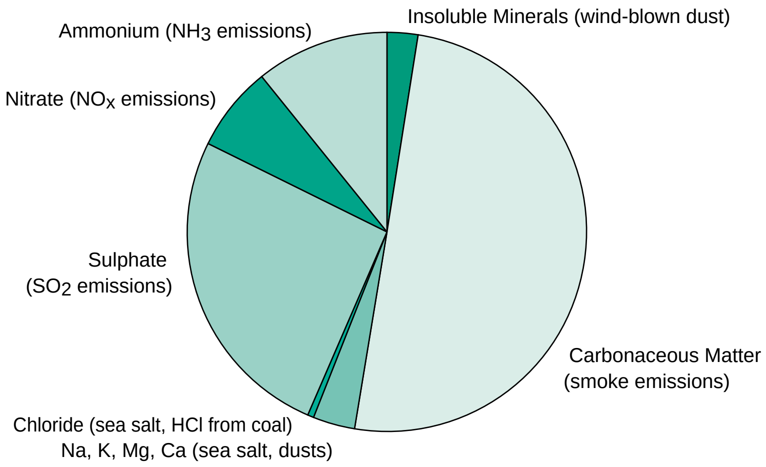
A typical approximate breakdown of UK particulate matter composition may be expressed as follows: ammonium ~5%, sulphate, nitrate and chloride ~30%, carbonaceous material ~40%, metals ~5% and insoluble material (minerals) ~20%. (QUARG, 1993). Figure 7.1 illustrates this graphically. This has been derived by combining data from several studies carried out in different places at different times using different techniques and so cannot be regarded as being especially rigorous. The trace heavy metals and specific organic compounds comprise a tiny percentage of the total mass, and it is these which have been covered by the most extensive sampling

Figure 7.1 Approximate Composition of Urban Particles.

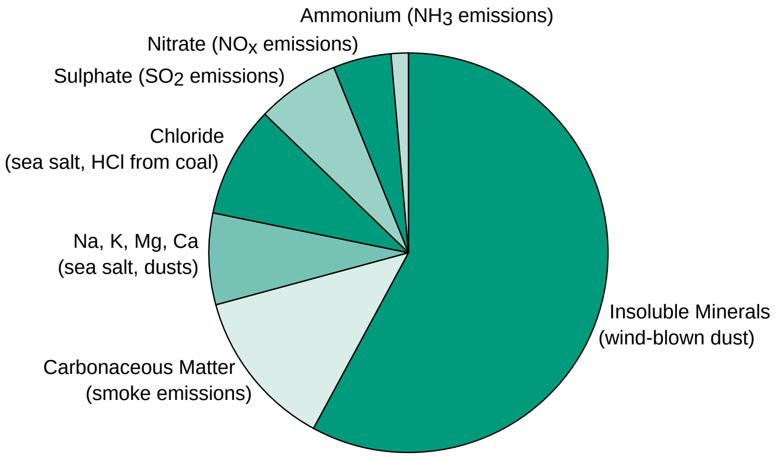
(a) Total



(b) Fine Fraction



(c) Coarse Fraction



campaigns. No survey covering all the components simultaneously has yet been carried out in the UK

7.2.1 Background on the Reported Studies

Leeds 1982

A study of rural and urban particulates was made by Clarke et al (1984) in the Leeds area. They used the dichotomous samplers described earlier. A series of 24 hour samples were taken between June and September 1982. Analysis was performed for SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-. As the filters were weighed to determine the total mass concentration in each fraction it is possible to express the concentration of each species as a percentage of the total mass. This study is consequently the most useful yet done in the UK, and the results derived have been used in other reviews (eg QUARG, 1993) as representative of urban exposures in general. It will thus be used as the main source of data for the soluble fraction, with other studies supplementing it.

Lancaster 1979-1981

Harrison and Pio (1983) describe a sampling campaign near Lancaster, in north-west England. The site is far from major urban regions so is representative of rural air. As the sea is 10 km away some of the samples were from maritime air masses. Twenty-four hour samples were taken using cascade impactors to provide a range of size selections which were analysed for 9 ionic species, including four metals (Ca, K, Na and Mg). The totals of measured nano-equivalent concentrations balanced to within 3% implying that these 9 species represented the vast majority of the soluble ionic fraction. This study covers the greatest number of ionic species and so provides the most information about the chemical combinations within the ionic material. Comparison with the Leeds data is meaningful if the cascade impactor ranges are grouped into two fractions corresponding to the fine and coarse dichotomous sampler ranges.

Lancaster 1978-1982

Colbeck and Harrison (1984) report measurements for sulphate, nitrate, and ammonium from five sampling periods at different locations in the Lancaster area. Size fractionation was not employed. Two of the campaigns involved simultaneous measurement at two sites giving information about the spatial distribution of the species. At one site the total suspended particulate (TSP) was measured allowing a rough estimate to be made of the percentage by mass contributed by each species.

Essex 1987-1988

Measurement of particulate NO_3^-, SO_4^{2-}, NH_4^+, and Cl^- were made by Harrison and Allen (1990) at a small network of sites in eastern England. No particle size discrimination was employed. In addition measurements were made of gaseous NH_3, HCl, and HNO_3. While detail is not given on these in this report they do give some useful insights into the sources of the particles.

Essex 1987-1989

The survey by Kitto and Harrison (1992a, b) in Essex to investigate processes affecting aerosol acidity involved taking weekly 24 hour samples at four sites, with three sites operated simultaneously. The concentration of strong acid was measured as well as those of the usual ionic species, allowing the amount of SO_4^{2-} present as sulphuric acid to be determined. The first three sites were sampled simultaneously between May and December 1987.

7.3 RESULTS OF REPORTED STUDIES

7.3.1 Sulphates

Leeds 1982

As expected the fine fraction concentrations (r=0.95, n=96) are better correlated between sites than the coarse (r=0.7, n=96). 85% of the sulphate occurs in the fine fraction, with both urban and rural sites having the same distribution between fractions. (Table 7.1).

Lancaster 1979-1981

The concentrations of sulphate were measured, and the results are shown in Table 7.2. Sulphate concentrations in the fine fraction, averaged over the period, were 7.9 µg/m^3. This represents about 34% by mass of the total soluble ionic fraction (calculated as a percentage of the averages, rather than an average of the percentages). Further investigation of the balance of nano-equivalent concentrations indicates that the sulphate is mostly present as ammonium sulphate, although some is present as sodium sulphate of marine origin. The latter occurs in particles with a mode of about 3.5 µm: this is in the coarse fraction, but the particles will still be partly respirable.

Lancaster 1978-1982

Only at Hazelrigg 1979-1981 were measurements made of the total sampled mass on the filter: in this case the mean Total Suspended Particulates (TSP), as defined earlier, was 39.24 µg/m³ with a range of 20.0 - 73.0 µg/m³. This indicates that sulphate was about 22% by mass of the TSP when calculated from the means, which is smaller than that found in Leeds.

Essex 1986-1987

Mean sulphate concentrations (µg/m³) are shown in Table 7.3. No calculation of the fraction of sulphate in the total soluble ionic species is made. The only cation measured is NH_4^+ so an accurate ion balance is not possible. However, an estimate based on the overall means shows that sulphate represents about 34-35% of the total sulphate, nitrate, chloride and ammonium fraction, which is in keeping with the value obtained in Lancaster for total soluble ions. Note that the Lancaster survey shows that these four species amount to about 91% by mass of the total soluble ionic fraction.

Essex 1987-1989

Linear regressions were performed between the three simultaneous sites which gave values of r^2 of between

Table 7.1 Sulphate Measurements from Leeds, 1982.

Site	Size Fraction	$[SO_4^{2-}]$ µg/m³ mean	% of Total Mass in Fraction	Number of samples
Leeds	**Fine**	5.8	26.1	97
(Urban)	**Coarse**	1.0	7.5	98
Haverah	**Fine**	5.3	30.8	111
Park	**Coarse**	0.9	9.3	111
(Rural)				

Table 7.2 Sulphate Measurements from Lancaster, 1979-1981.

Site	Period	Mean Sulphate Concentration µg/m³	Range µg/m³	Standard Deviation
Heysham	31/5/78 - 1/9/78	8.37	0.1-38.4	7.41
Hazelrigg	23/10/78 - 22/11/78	6.71	0.3-21.6	6.39
Lancaster, Town Hall	23/10/78 - 22/11/78	7.27	1.2-21.1	6.47
Hazelrigg	1979 - 1981	8.78	1.6-52.2	8.12
Lancaster,Town Hall	24/9/79 - 24/10/79	9.23	1.1-33.1	7.70
Cockerham	24/9/79 - 24/10/79	6.01	0.3-22.9	5.44
Stodday	4/5/82 - 1/9/82	5.12	0.7-24.3	5.30

Table 7.3 Sulphate Measurements (µg/m³) from Essex, 1986-1987.

Period	Essex University	Colchester	Dedham	Walton Pier	Overall Mean (all sites)
21.8.86 - 13.11.86	3.46	3.44	3.75	3.22	3.47
24.2.87 - 16.4.87	9.34	10.70	9.28	8.47	9.45

0.92 and 0.96 for sulphate concentrations. Such uniform spatial distributions are consistent with sulphate being found in the "fine" fraction (Table 7.4).

Conclusions from the Sulphate Studies

Sulphate consistently appears to account for about 30-35% by mass of the soluble ionic fraction. Where the total mass has been measured it is ~25% of the mass of the fine fraction, although studies employing size discrimination do not do this in a consistent way. Sulphate levels demonstrate good spatial uniformity, fitting in with their likely origins as fine particles of ammonium sulphate formed as secondary aerosol in the atmosphere. The evidence from the ionic balance studies, especially Harrison and Pio (1983), points to sulphate being associated with NH_4^+ as the predominant cation. It may thus be present as fully neutralised $(NH_4)_2SO_4$ or as acidic NH_4HSO_4 or H_2SO_4 dependent upon the extent of neutralisation by ammonia.

7.3.2 Aerosol Acid

While sulphate is usually largely present as a neutral salt, some concern has arisen about the effects on health of acid aerosol, the majority of which is expected to be ammonium bisulphate or sulphuric acid (Radojevic and Harrison, 1992). Few measurements have been made of the concentration of H^+. The study in Essex during 1987-89 (Kitto and Harrison, 1992b) investigated the processes affecting strong acid concentrations. The concentrations of strong acid were usually very small: ~0-178 neq/m³, atmospheric NH_3 is usually present in sufficient quantities to neutralise any H^+ present (Table 7.5). The typically low concentrations usually found when expressed in μg/m³ can give a misleading impression of the importance of H^+. Because the molecular mass is small the percentage of H^+ in the total ionic fraction is far greater when the concentrations are expressed in chemical equivalents, which gives a more realistic measure of the amount of H^+ available for reaction.

7.3.3 Ammonium Compounds

All the studies quoted where sulphate was measured also give values for ammonium concentrations. As before the Leeds study can be considered the most useful (Table 7.6).

Leeds 1982

The correlation between the fine fraction concentrations at the two sites was 0.97 for 44 samples. Very little is found in the coarse fraction:

Table 7.4 Sulphate Measurements from Essex, 1987-1989.

	Walton Pier	**Essex University**	**Great Domsey**	**Essex University 2**	**Ardleigh (Day)**	**Ardleigh (Night)**
Sampling Period	**May - Dec 1987**	**May - Dec 1987**	**May - Dec 1987**	**March - Dec 1987**	**May - July 1989**	**May - July 1989**
Mean $[SO_4^{2-}]$ μg/m³	5.7	5.4	5.8	8.3	8.5	6.9
Standard Deviation	4.6	4.4	4.8	8.1	7.6	6.0

Table 7.5 Aerosol Strong Acid Measurements, 1987-1989.

	Walton Pier	**Essex University**	**Great Domsey**	**Essex University 2**	**Ardleigh (Day)**	**Ardleigh (Night)**
Sampling Period	**May - Dec 1987**	**May - Dec 1987**	**May - Dec 1987**	**March - Dec 1987**	**May - July 1989**	**May - July 1989**
Mean $[H^+]$ μg/m³	0.029	0.018	0.012	0.017	0.018	0.014

often zero to within the experimental error. This is not surprising since, as explained earlier, the coarse particles are predominantly mineral materials which, being alkaline, would not react with gaseous ammonia. The correlations between fine NH_4^+ and fine SO_4^{2-} were found to be 0.99 at both sites, fitting the expected pattern of the fine particles being largely composed of ammonium sulphate formed through reaction in the atmosphere.

Lancaster 1979-1981

Ammonium concentrations averaged 4.2 µg/m³ over the period. This represents 18.2% by mass of the soluble ionic fraction. Once again virtually all was present in the fine fraction. As this is the only study where a cascade impactor was used it provides useful information on the size distribution of the particles. The bulk of ammonium, together with sulphate and nitrates, occurs in particles between 0.05 and 2 µm in diameter.

Lancaster 1978-1982

Ammonium was measured at three of the five sites used by Colbeck and Harrison (1984). Concentrations arte shown in Table 7.7. This represented between 20 and 23% by mass of the of the measured soluble ions: NH_4^+, SO_4^{2-}, and NO_3^-. Given that the other Lancaster study indicated that these three species contribute nearly 80% of the soluble mass then it could be estimated that this represents about 18% of the total soluble ionic material, a figure which fits with the other study.

Essex 1986-1987

Ammonium concentrations are shown in Table 7.8. The overall mean concentration of ammonium was 26% of the soluble fraction in the first campaign, and 21% in the second.

Essex 1987-1989

As only sulphate and ammonium were measured it is not possible to calculate a percentage of the soluble fraction, or total mass (Table 7.9).

Conclusions from the Ammonium Studies

Ammonium accounts for between about 18 to 25% of the soluble ionic fraction of particulate matter. It is almost entirely confined to the fine fraction where it is present as chlorides, sulphates and nitrates formed

Table 7.6 Ammonium Measurements from Leeds, 1982.

Site	Size Fraction	$[NH_4^+]$ µg/m³	% of Total Mass in Fraction	Number of Samples
Leeds	**Fine**	2.2	9.9	45
(Urban)	**Coarse**	0.2	1.5	45
Haverah				
Park	**Fine**	2.3	13.4	60
(Rural)	**Coarse**	0.3	3.1	60

Table 7.7 Ammonium Measurements from Lancaster, 1978-1982.

Site	Period	Mean Ammonium Concentration µg/m³	Range µg/m³	Standard Deviation µg/m³
Heysham	31/5/78 - 1/9/78	3.18	0.1-11.5	2.39
Hazelrigg	1979 - 1981	4.32	0.2-26.2	4.13
Stodday	4/5/82 - 1/9/82	2.07	0.1-9.9	2.26

Table 7.8 Ammonium Measurements from Essex, 1986-1987.

Period	Essex University µg/m³	Colchester µg/m³	Dedham µg/m³	Walton Pier µg/m³	Overall mean (all Sites) µg/m³
21.8.86 - 13.11.86	2.62	2.48	3.21	2.34	2.66
24.2.87 - 16.4.87	5.76	5.89	5.75	5.13	5.63

Table 7.9 Ammonium Measurements from Essex, 1987-1989.

	Walton Pier	**Essex University**	**Great Domsey**	**Essex University 2**	**Ardleigh (Day)**	**Ardleigh (Night)**
Sampling Period	**May - Dec 1987**	**May - Dec 1987**	**May - Dec 1987**	**March - Dec 1987**	**May - July 1989**	**May - July 1989**
Mean [NH_4^+] µg/m^3	2.7	3.0	3.3	5.3	3.9	4.5
Standard Deviation µg/m^3	2.4	2.4	2.8	5.4	3.4	3.4

Table 7.10 Nitrate Measurements from Leeds, 1982.

Site	**Size Fraction**	**[NO_3^-] µg/m^3**	**% of Total Mass in Fraction**	**Number of Samples**
Leeds (Urban)	**Fine**	1.9	8.5	97
	Coarse	0.9	6.8	97
Haverah Park (Rural)	**Fine**	1.7	9.7	111
	Coarse	1.1	11.3	111

Table 7.11 Nitrate Measurements from Lancaster, 1978-1982.

Site	**Period**	**Mean nitrate concentration µg/m^3**	**Range µg/m^3**	**Standard deviation µg/m^3**
Heysham	31/5/78 - 1/9/78	3.19	0.2-12.8	3.18
Hazelrigg	23/10/78 - 22/11/78	5.53	0.7-14.2	4.11
Lancaster, Town Hall	23/10/78 - 22/11/78	5.96	0.3-15.2	4.49
Hazelrigg	1979 - 1981	5.45	0.6-20.2	5.04
Lancaster,Town Hall	24/9/79 - 24/10/79	3.6	0.1-13.4	3.17
Cockerham	24/9/79 - 24/10/79	5.03	0.1-16.7	4.57
Stodday	4/5/82 - 1/9/82	2.68	0.1-11.2	2.87

through reaction in the atmosphere between ammonia and acid gases originating from pollution sources.

7.3.4 Nitrates

Leeds 1982

Nitrate was found to be 7.5% to 8.5% of the fine fraction, and the fine fraction represented the majority of the nitrate (68% in Leeds, 61% Haverah Park); (Table 7.10).

Lancaster 1978-1982

Nitrate comprised 25-29% of three major ionic species NH_4^+, SO_4^{2-}, NO_3^- (Table 7.11).

Essex 1986-1987

Nitrate was found to be about 25-39% of the total nitrate, sulphate, ammonium and chloride fraction. (Table 7.12).

Conclusions from the Nitrate Studies

Nitrate represents about 25% of the total soluble ionic fraction, mostly confined to the fine fraction, although

Table 7.12 Nitrate Measurements from Essex, 1986-1987.

Period	Essex University	Colchester	Dedham	Walton Pier	Overall Mean (All Sites)
	μg/m³	μg/m³	μg/m³	μg/m³	μg/m³
21.8.86 - 13.11.86	3.06	2.74	3.53	2.96	3.07
24.2.87 - 16.4.87	9.14	9.84	8.96	8.21	9.04

Table 7.13 Chloride Measurements from Leeds, 1982.

Site	Size Fraction	$[Cl^-]$ μg/m³	% of Total Mass in Fraction	Number of Samples
Leeds	Fine	0.4	1.8	97
(Urban)	Coarse	1.1	8.2	97
Haverah Park	Fine	0.2	1.2	111
(Rural)	Coarse	0.9	9.3	111

Table 7.14 Chloride Measurements from Essex, 1986-1987.

Period	Essex University	Colchester	Dedham	Walton Pier	Overall Mean (All Sites)
	μg/m³	μg/m³	μg/m³	μg/m³	μg/m³
21.8.86 - 13.11.86	0.89	1.06	1.28	1.13	1.09
24.2.87 - 16.4.87	2.27	3.06	2.31	2.39	2.51

this association is less clear-cut with nitrates than sulphates. The bulk is probably in the form of ammonium nitrate, with some sodium nitrate.

7.3.5 Chloride

Leeds 1982

Results obtained are in Table 7.13

Lancaster 1979-1981

Harrison and Pio record Cl^- concentrations of 2.9±1.6 μg/m³, 12.9% of the soluble fraction..

Essex 1986-1987

Data appear in Table 7.14

Conclusions from Chloride Studies

Two distinct contributors of chloride appear to be present. The majority is in the coarse fraction where marine aerosol is present; here it is mainly sodium chloride, with some ammonium chloride. In the fine fraction, chloride is formed from gaseous HCl originating from pollution and is usually ammonium chloride. Note that all the areas described above are subject to considerable influence from marine aerosol. None of the campaigns covered any of the largest conurbations in Britain, but it would be expected that samples taken in coastal areas would contain far larger fractions of sea salt than an inland conurbation like the West Midlands. A second source of salt is the grit used for de-icing roads in winter. Again this is expected to appear as higher chloride concentrations in the coarse fraction in winter. While size discrimination was not applied during the Essex 1987-88 study it is clear that samples taken during the winter period contained up to three times the chloride found during the late summer and autumn.

Chemical Associations of Soluble Ionic Species

A few studies have sought to identify which chemical cations and anions are associated with one another in airborne particles. The most common and clear associations are as follows:

Sulphate is predominantly present as $(NH_4)_2SO_4$ with lesser amounts of NH_4HSO_4 and H_2SO_4.

Nitrate is present as NH_4NO_3, with some $NaNO_3$

Chloride is mainly NaCl close to coasts, with NH_4Cl predominating inland.

Ammonium is combined with sulphate, nitrate and chloride.

Sodium is mostly bound with chloride, with some nitrate and sulphate.

Calcium is largely present as sulphate or carbonate.

Magnesium is associated with chloride in coastal regions, and with carbonates in areas with dolomitic geology.

Spatial and Temporal Changes in Secondary Aerosol Components

There is a spatial trend in annual average sulphate aerosol across the United Kingdom with highest concentrations in the south and east, declining towards the north-west of Britain. This trend is expected to apply also to nitrate and ammonium concentrations. There is also a seasonal pattern with slightly higher concentrations of sulphate observed in the summer months. These are illustrated diagrammatically in Chapter 8.

Most of the data presented to date have been annual means, and short-term excursions to far higher concentrations may be observed. The ranges indicated, for example, for the Lancaster area in 1978-82 show 24 hour average sulphate reaching up to 52 $\mu g/m^3$ with nitrate up to 20 $\mu g/m^3$. Peak to mean ratios for 24-hour samples were thus up to 5.9 and 3.7 for sulphate and nitrate respectively. Data collected at Harwell in 1971 (Atkins et al, 1972) show hourly average sulphate concentrations reaching 70 $\mu g/m^3$ in a pollution episode. It is unlikely that sulphate would now reach such high levels due to a general reduction in sulphur dioxide emissions across Europe.

7.3.6 Metals

Metals are present from both natural and anthropogenic sources. For some species, especially sodium and magnesium which are present in sea water, the natural sources are dominant. Unlike the trace metals, those of marine origin will be found almost entirely in the soluble ionic fraction. For others, especially heavy metals in urban areas, anthopogenic sources dominate. Industrial emissions of metals arise mainly from condensation and are more likely to appear in the fine fraction. Fine particles have a greater probability of escaping emission controls and are capable of greater travel distances in the atmosphere. There is some tendency for metals to condense onto the surface of other small particles as the surface area/mass ratio increases with decreasing size. It is therefore possible for fine particles to disperse widely from their source and to present a respiratory health hazard. This has provided the stimulus for a number of extensive UK trace metals sampling programmes.

Analyses of Metal Concentrations

Sources of data range from small scale research projects to national sampling campaigns designed to monitor compliance with air quality standards. National campaigns have the advantage of covering a number of sites with a standardised analytical method and strict quality control procedures. The studies summarised here include that carried out in Lancaster by Harrison and Pio (1983), where major metallic species were measured in the soluble ionic fraction; Harrison and Williams (1982) where a larger number of metals were investigated at the same sites, and a brief discussion of roadside deposition from a study by Harrison and Johnston (1985). The most extensive source of data is the Department of the Environment’s (DoE) Multi-Element Survey undertaken by Warren Spring Laboratory (WSL)(McInnes, 1990) whose objectives are to provide data on the concentrations and trends of trace elements in the urban areas across the UK. A study by AEA-Technology which includes both urban and rural sites also provides a substantial long-term dataset (Lee et al, 1994).

Sodium, Magnesium, Potassium and Calcium

As part of the Lancaster survey of ionic species described earlier, analysis was performed for four metals. Na and Mg would be expected to be present in relatively large amounts owing to the presence of maritime air masses and proximity to the coast. The results are shown in Table 7.15.

Table 7.15 Measurements of Major Ion Metals, Lancaster, 1978-1982.

	$[Ca^{2+}]$	$[K^{+}]$	$[Na^{+}]$	$[Mg^{2+}]$
Mean concentration (µg/m^3)	0.400	0.196	1.288	0.146
Standard deviation (µg/m^3)	0.200	0.117	0.713	0.073
Mean Proportion in Fine Fraction (%)	25	44	21	19
% Mass of Total Ionic Fraction	1.8	0.8	5.6	0.6
Arithmetic Mean of Median Diameters (µm)	6.0		5.4	

TABLE 7.16 Trace Metal Concentrations Measured in Central London Between 1984/5 and 1992/3 (ng/m^3) (from DoE, 1995).

	1984/5	1985/6	1986/7	1987/8	1988/9	1989/90	1990/1	1991/2	1992/3
Cadmium	2.8	3.6	2.7	7.2	16.0	4.8	(1.3)	<1	0.4
Chromium	12	5.5	10	14	15	11	(4.3)	6	5.4
Copper	27	27	..	32	34	25	(28)	24	13
Iron	980	840	940	1,000	1,100	1,140	(1,687)	913	891
Manganese	19	18	17	18	18	20	25	15	21
Nickel	17	7.8	8.6	8.8	10	8.9	(8.6)	5	5.2
Zinc	100	94	93	94	120	111	(139)	65	59
Vanadium	32	14	14	14	16	15	(20)	15	12
Colbalt	..	..	..	..	2.2	0.8	(0.8)	-	0.3
Lead	480	270	280	300	220	..	120	99	78

Note: Figures in parentheses refer to < 75% data capture.

In contrast with the other ionic species, these metals are mostly found in the coarse fraction. This would be predicted from their origins in sea spray and terrestrial dusts which exist mainly as larger particles. The sodium is present mainly as sodium chloride and sulphate.

Trace Metals

The Multi-Element Survey has been in operation since 1976 as part of the National Survey of Air Pollution. Twenty urban sites were chosen initially, reduced after two years to the five which most frequently experienced above-average concentrations of several of the elements being monitored. As a consequence they probably represent the extreme rather than typical concentrations. For this reason the results obtained from *ad-hoc* research projects provide a useful comparison. The samples are not size fractionated, but it would be expected that most trace metals will be present in the fine fraction.

A summary of the results for Central London between 1984/5 and 1992/3 is given in Table 7.16; this illustrates the trends in each element and in general displays a reduction. Lead shows considerable reductions resulting firstly from reductions in the lead content of petrol, and subsequently the increased market penetration of unleaded petrol. The Multi-Element survey monitored metal levels in areas with industrial metal sources and heavy urbanisation. This is based upon the reasonable assumption that industrial point sources are responsible for much of the emissions. In this respect lead behaves somewhat differently from the other metals. Emissions from petrol combustion far exceed industrial "point sources" so lead concentrations are in most instances dependent on proximity to roads and the traffic volume on the road. A study by Harrison and Johnston (1985) investigated lead *deposition* as a function of distance from the M6 in NW England. Although deposition rate is not an exactly equivalent measure to concentration, the results do illustrate clearly the significance of proximity. At the immediate roadside the deposition rate was nearly 12 mg/m^2/week, this had halved by 10 metres away and virtually levelled off at about 0.5 mg/m^2/week at 20 m. To monitor the effects of the policies to reduce vehicle lead emissions some monitoring has been carried out specifically at roadsides. While the Multi-Element survey has recorded no breaches of the WHO guidelines for lead (0.5-2 µg/m^3) since 1986, the WSL "Lead in Petrol" survey recorded roadside levels which exceeded the guideline limits up until 1989 in Cardiff and Manchester (QUARG, 1993). All sites show lead levels to be falling.

The AEA-Technology survey (Lee et al, 1994) involved two sampling sites in Greater London, four in Greater Manchester, an industrial site in Walsall (excluded from the data in this review), and two rural sites. Mean concentrations at urban and rural sites over the period 1986-1989 appear in Table 7.17, together with the reduction from concentrations measured in 1975-1978. For pollutants measured in both this survey and the WSL Multi-Element survey, urban concentrations are similar. There is, however, a limited overlap of elements, and the two surveys are largely complementary.

Lancaster 1978-1981

Harrison and Williams (1982) made a comparison between urban and rural concentrations of lead, cadmium and zinc. The "urban" area, Lancaster, does not have significant industrial sources so any metals found within will either be from traffic or have been brought in from other areas. As the samples were taken between 1978 and 1979, since when all the metal concentrations have fallen, the results should be used for comparison with contemporary data rather than considered to represent today's values. It should also be noted that while the data given for the multi-element survey were annual averages, the values given by Harrison and Williams are from 24 hour and 7 day samples (Table 7.18).

Table 7.18 Trace Metal Measurements from Lancaster, 1978-1981.

Metal	Mean Concentration (ng/m^3)
Cadmium	1.17 - 2.00
Zinc	62 - 91 (rural), 139 - 160 (urban)
Lead	132 - 228 (rural), 3400 - 3770 (urban)

All these (except lead) are consistently lower than the values found for the urban areas used as sites in the Multi-Element Survey in 1978/79, confirming that the Multi-Element Survey is generally representative of the more heavily polluted locations.

7.3.7 Carbon Compounds

Carbonaceous material, which comprises about 25-50% of the fine fraction, is mainly derived from

TABLE 7.17 Summary of Data from AEA-Technology Trace Element Survey (Lee et al, 1994).

	URBAN		RURAL	
Element	**Mean Concn 1986-1989 (ng/m^3)**	**Reduction from 1975-1978 (%)**	**Mean Concn 1986-1989 (ng/m^3)**	**Reduction from 1975-1978 (%)**
Bromine	72.9	65	19.2	42
Zinc	87.0	54	30.0	59
Lead	183	69	33.4	61
Aluminium	456	35	160	28
Iron	623	36	152	46
Chromium	5.6	34	0.95	57
Arsenic	2.65	74	1.32	56
Cadmium	2.0	74	0.76	60
Nickel	9.0	50	1.6	68
Vanadium	14.7	60	4.5	53
Mercury	0.14	42	0.047	7
Silver	0.26	63	0.070	79
Cerium	0.63	51	0.254	43
Selenium	2.0	32	0.97	36
Samarium	0.05	53	0.018	45
Scandium	0.10	45	0.036	49

"smoke" particles (i.e. the products of incomplete combustion). There are three main forms in which carbon compounds occur:

carbonate: normally less than 5% of the total mass, includes soil derived minerals, and hence is present mainly in the coarse fractions;

organic carbon: normally about 60-80% of total carbon, includes some compounds with potential carcinogenic effects; and

particulate elemental carbon (PEC): which is the black component responsible for the soiling characteristics of particulate matter.

Both organic carbon and PEC are major constituents in smoke from incomplete combustion processes. "Black Smoke", as defined by a British Standard, was for many years the only measurement of particulate matter made on a national scale. The method is based upon measuring the reflectance of a filter through which air has been drawn for 24 hours. The particulate loading is calculated from the reflectance by a calibration curve produced empirically in the 1950s. The coal smoke which predominated then has now been replaced by darker smoke from combustion of oil products, chiefly diesel vehicle fuel. Annual means for the "pollution year" 1992-93 varied between 11 µg/m^3 (Cardiff and Birmingham) and 17 µg/m^3 (Belfast). The British black smoke sampler has been found to exhibit a 50% size cut-off at 4.4 µm so will collect predominantly fine particles (McFarland, 1992).

Elemental Carbon (PEC)

Few measurements of PEC have been made in the UK The majority of the soiling associated with "black smoke" is due to elemental carbon which has been inferred from reflectance methods, (Edwards et al, 1983). A measurement programme for PEC in Leeds gave levels of about 6 µg/m^3. Recent measurements in Birmingham (Pio et al, 1994) have indicated a mean of ca 3 µg/m^3 corresponding to about 10% of PM_{10} mass.

Organic Carbon

The organic fraction contains a vast range of organic chemicals most of which are produced in combustion processes or formed by chemical reactions in the atmosphere. Total organic carbon concentrations in Birmingham are ca 5 µg/m^3, about 15% of PM_{10} mass (Pio et al, 1994). Toxic organic micropollutants (TOMPs) are not confined to particles, but are also present in gaseous form. The main types which are commonly measured are dioxins (polychlorinated dibenzo-p-dioxins), PCBs (polychlorinated biphenyls), and PAH (polynuclear aromatic hydrocarbons). There are very many other organic compounds present in UK airborne particles, but few, if any, measurements exist, even of a qualitative nature.

The most useful source of data on these is from the UK Department of Environment TOMPs network for which preliminary data are available (Clayton et al, 1992). Four sites were originally operated at Cardiff, London, Manchester and Stevenage. More recently, Stevenage has closed and has been replaced by sites at Middlesbrough and Lancaster. Measurements were made both of concentration in the air and deposition rates. The former will measure the suspended particulates, predominantly of small diameter, while the deposition rates are influenced more by the larger particles which will have shorter lifetimes. Additional studies of PAH only have been made in London by Baek (1992) and in Birmingham (Smith and Harrison, 1994).

Polychlorinated Dioxins and Furans

Table 7.19 summarises the dioxin/furan measurements at UK TOMPs sites in 1993, expressed as toxic equivalent (TEQ). Figure 7.2 describes the breakdown of congeners by actual mass.

Polychlorinated Biphenyls

The average PCB concentration in London in 1991 was 1474 pg/m^3 which breaks down into components as shown in Figure 7.3. Table 7.19 includes the average concentration of total measured PCBs at five sites in 1993.

Polynuclear Aromatic Hydrocarbons

Table 7.19 includes also the total of measured PAH (acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(ghi)perylene) at the five TOMPs sites during 1993. Table 7.20 gives a breakdown by compound at various UK sites, including also the vapour phase component.

7.3.8 Minerals

When the soluble inorganic compounds have been quantified, and the carbonaceous fraction accounted for, about 20-25% of the mass of urban particulate matter remains unidentifiable. This is the insoluble mineral fraction. Identification of individual elements within this fraction is possible using such techniques

Table 7.19 Mean Concentrations of Toxic Organic Micropollutants at UK Sites, 1993 (From DoE, 1995).

Site	**Mean Dioxin (fg TEQ/m³)**	**Mean PCB (pg/m³)**	**Mean PAH (ng/m³)**
London	169	1165	120
Manchester	294	463	70
Cardiff *	206	552	56
Middlesbrough	240	213	143
Lancaster	132	87	232

* Cardiff annual mean for 1992.

Figure 7.2 Distribution of Dioxin Congeners by Mass for London (1991).

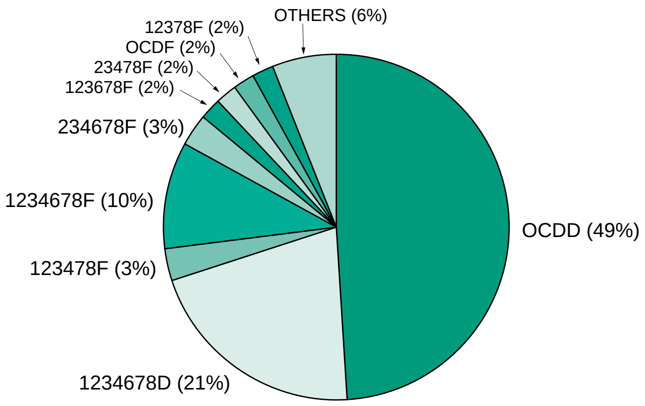


Figure 7.3 Distribution of PCB Congeners by Mass for UK TOMPS Network Sites for 1991.

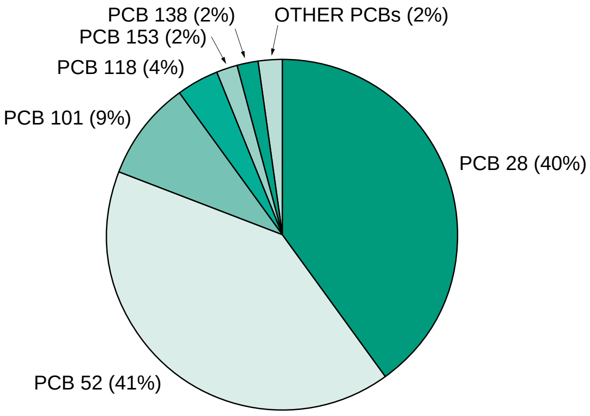


TABLE 7.20 Average PAH Concentrations (ng/m^3) for South Kensington, Birmingham and Manchester (From QUARG, 1993).

	South Kensington(a)		Birmingham(b)		Manchester(c)	
	Particulate	**Vapour**	**Particulate**	**Vapour**	**Particulate**	**Vapour**
Naphthalene	-	-	0.21	13.0	-	-
Acenapthylene	-	-	0.61	14.8	-	-
Fluorene	-	-	1.1	12.6	0.5	26.0
Acenaphthene	-	-	1.6	11.9	ND	1.2
Phenanthrene	0.11	5.01	1.1	23.0	0.4	56.7
Anthracene	0.18	2.66	0.4	4.1	0.05	4.7
Fluoranthene	0.81	2.65	1.2	11.2	0.63	16.2
Pyrene	0.79	3.00	2.4	35.6	0.8	10.7
Benzo[c]phenanthrene	0.85	1.98	-	-	-	-
Cyclo[c,d]pyrene	2.61	1.47	-	-	-	-
Benzo[a]anthracene	0.79	0.62	1.5	4.1	1.0	0.5
Chrysene	1.22	0.40	2.2	4.3	1.8	1.6
Benzo[b]fluoranthene	0.98	0.24	-	-	-	-
Benzo[e]pyrene	2.00	0.31	-	-	-	-
Benzo[b]fluoranthene	1.61	0.17	2.0	0.19	2.4	ND
Benzo[k]fluoranthene	0.68	0.07	1.1	0.08	2.4	0.03
Benzo[a]pyrene	1.44	0.19	0.73	0.08	1.6	ND
Dibenzo[a,h]anthracene	0.12	ND	0.79	0.04	-	-
Benzo[g,h,i]perylene	3.30	0.01	1.9	0.06	3.1	0.02
Indeno[1,2,3,c,d]pyrene	1.57	ND	2.0	ND	-	-
Anthanthrene	0.63	ND	-	-	-	-
Coronene	1.67	ND	1.0	ND	1.4	ND

(a) annual average;
(b) average of 27 daily samples, February 1992;
(c) results for week 7, 1992, Manchester TOMPS site.

as PIXE (Proton Induced X-Ray Emission) or X-Ray Fluorescence (XRF) which can provide an accurate multi-species breakdown of an aerosol sample on the filter paper (Rashiduzzaman, 1981). However, these techniques give no indication of the chemical speciation and associations of the elements. One approach is to use X-Ray Powder Diffraction (XRD) which can provide a semi-quantitative estimation of individual crystalline substances. Sturges et al (1989) describe semi-quantitative XRD analysis of size-fractionated samples. Unfortunately the technique has not been widely applied in the UK, but a comparison of a number of worldwide studies indicates that many of the components are found to be common to all. In general, XRD analysis finds about 50% of the total aerosol mass to be identifiable, about half of which is in the soluble inorganic fraction, and half is minerals. The former have included NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_2SO_4.2NH_4NO_3$, and $(NH_4)_2SO_4.3NH_4NO_3$, which occur mostly in the fine fraction. Sodium compounds from sea spray appear in the coarse fraction, along with insoluble minerals blown from soils or industrial grinding operations. A list of compounds identified in UK air samples by XRD appears in Table 7.21. No UK study has been quantitative, hence the Table includes all those compounds which were above the detection limit (about 1% of mass).

Studies carried out worldwide produced a large number of species (QUARG 1993, Sturges et al, 1989) including many clay minerals. A study in Toronto found more species than those identified by the UK studies, including dolomite, feldspar, chlorite, kaolinite and magnetite. The precise composition is highly dependent on local geology, especially for the coarse particle fraction.

TABLE 7.21 Compounds Identified in UK Urban Air Using X-Ray Powder Diffraction.

NATURAL MINERALS

α-Quartz (SiO_2)
Calcite ($CaCO_3$)
Epsomite ($MgSO_4.7H_2O$)
Gypsum ($CaSO_4.2H_2O$)
Feldspar ($KAlSi_3O_8$)
Chlorite)
Kaolinite) clay minerals
Montmorillonite)

LEAD COMPOUNDS (from leaded petrol)

$PbSO_4.(NH_4)_2SO_4$
$PbSO_4$
$PbBrCl$

AMMONIUM SALTS

$(NH_4)_2SO_4$
NH_4HSO_4
NH_4NO_3
NH_4Cl
$(NH_4)_2SO_4.2NH_4NO_3$
$(NH_4)_2SO_4.3NH_4NO_3$

SULPHATES

$CaSO_4.(NH_4)_2SO_4.H_2O$
$Na_2SO_4.NaNO_3.H_2O$
$Na_2SO_4.(NH_4)_2SO_4.4H_2O$
$Fe_2(SO_4)_3.3(NH_4)_2SO_4$

SEA SALT/ROAD SALT

$NaCl$

7.4 DATA SUMMARY

The results obtained from various urban studies are summarised in Table 7.22. The range of values which are found for each parameter is very large so these figures are chiefly intended to provide an indication of the order of magnitude concentrations found in urban areas. Where possible an estimate is given for the percentage of the total mass which each species represents. It is not always possible to do this in a rigorous manner because the majority of workers have not measured the total collected mass on their filters. The fourth column, "Percentage Found in Fine Fraction", shows how each species is distributed between coarse and fine fractions, a statistic which can tell a great deal about the likely sources and health implications. The first two indicators - PM_{10} and TSP (defined earlier) - are to give an indication of the typical mass concentrations for these two gravimetrically determined measures of particulate matter.

The information on soluble ionic species has been derived entirely from research undertaken by academic institutions. National monitoring networks provide the most comprehensive data on trace metals and toxic organic micropollutants, although a few other research groups do investigate PAH. It is the surveys which analyse for the greatest number of species simultaneously which are of most use - this was one of the considerations used when the table was compiled. Least is known about the organic carbon and insoluble inorganic fractions. The latter can be studied by X-Ray Powder Diffraction, but very little published data is available for the UK, and none is quantitative.

7.5 CONCLUSIONS

No comprehensive multi-species analysis, covering all the main fractions of airborne particulate matter, has been performed in Britain. National surveys measure either bulk properties like PM_{10} or black smoke; chemical analysis is confined to a few trace species, chiefly those associated with health hazards. Information on major species, especially soluble ionic ones, is available from a number of *ad-hoc* studies by academic institutions. The extent to which these may be compared is limited by differences between sampling and analytical procedures. The measurement programmes have tended to neglect the urban environment. As a consequence, a rigorous fractional breakdown of urban particulate matter can only be made when comprehensive multi-species analysis is performed in a number of urban centres, covering both inland and coastal sites.

Certain conclusions can be made with reasonable conviction from the available data. The coarse fraction is mostly natural in origin, the fine fraction predominantly anthropogenic. Most soluble ionic species are confined to the fine fraction and are

TABLE 7.22 Representative Concentrations of Individual Chemical Components of Airborne Particulate Matter.

Analyte	**Typical Concentrations**	**Typical Fraction of Total**	**Percentage Found in Fine Fraction**
PM_{10}	30 $\mu g/m^3$	N/A	~60%
TSP	35 $\mu g/m^3$	N/A	
Soluble Ionic Species:			
Sulphate	5-10 $\mu g/m^3$	20-25%	~85%
Nitrate	2-10 $\mu g/m^3$	10-20%	60-70%
Chloride	1-3 $\mu g/m^3$	<10%*	~10%
Ammonium	2-6 $\mu g/m^3$	<15%	>95%
Strong Acid (H^+)	0.02 $\mu g/m^3$	Trace	~100%
Carbonaceous:			
Elemental Carbon	3 $\mu g/m^3$	10%	~80%
Organic Carbon	5 $\mu g/m^3$	15%	~80%
Minerals:			
Natural Minerals	~8 $\mu g/m^3$	20-25%	~5%
Metals:			
Sodium	1 $\mu g/m^3$	2%*	21%
Magnesium	0.1 $\mu g/m^3$	0.2%*	19%
Calcium	0.4 $\mu g/m^3$	0.8%*	25%
Potassium	0.1 $\mu g/m^3$	0.2%*	44%
Lead	0.1 $\mu g/m^3$	0.2%	~90%
Other Trace Metals	5-50 ng/m^3	Trace	Most
Iron	0.5 $\mu g/m^3$	1%	35%
Toxic Organic Micropollutants:			
Dioxins	~200 fg TEQ/m^3	Trace	Most
PCBs	~1 ng/m^3	Trace	Most
PAH	~150 ng/m^3	Trace	Most

*Footnote: Surveys carried out in areas with abnormally high marine aerosol.

formed from neutralisation by ammonia of acid polluting gases like HCl, SO_2 and NO_2. Chloride is present in both coarse and fine fractions: as ammonium chloride in the fine, and as sodium chloride from sea-salt in the coarse. Carbonaceous (sooty) material is the other main component of the fine fraction.

Most of the organic material originates from combustion processes and is found in the fine fraction. With the exception of trace species of health concern, the organic fraction is very poorly characterised. Most of the metals are pollution-derived, and found in the fine fraction, except for sodium, calcium, magnesium and potassium which are marine or soil-derived in origin and found as soluble ions in the coarse fraction. Compared to knowledge of the organic fraction, trace metal concentrations in UK urban air are rather well characterised.

7.6 KEY POINTS

- *No recent comprehensive single-site data for the chemical composition of UK urban particles are available.*

- *It is possible to assemble a view of typical composition based on a review of data from many studies.*

- *The coarse fraction is mainly derived from soil, dust, and marine particles, the relative amounts depending on location. The elements calcium and potassium are strongly associated with the former* *sources, sodium, magnesium and chlorine with the latter.*

- *Ammonium sulphate and nitrate comprise a major part of the fine fraction particles. A small amount of ammonium chloride may also be present.*
- *Carbonaceous (sooty) material is the other major component of the fine fraction.*
- *There are many trace metals such as lead, cadmium etc associated with the fine fraction of airborne particles.*
- *The organic fraction of airborne particles is rather poorly characterised. Good data are available for dioxins/furans, PCBs and polycyclic aromatic hydrocarbons, but not in general for other components.*

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8 Receptor Modelling and Source Apportionment

8.1 INTRODUCTION

Effective strategies for control of airborne particulate matter must depend upon a sound knowledge of the sources of particulate matter in the atmosphere. There are essentially two approaches to the provision of that information: source inventories and receptor modelling. As outlined in Chapter 4, for sources such as road traffic which are readily quantifiable, source inventories can provide a reliable estimate of the magnitude of emissions. However, there are other emissions which depend in a less definite manner upon the quantity of the fuel or material used or the number of miles driven. For these, it may be extremely difficult to estimate the magnitude of emissions using the usual techniques of the inventory. Examples of this category are wind blown soil, street dust resuspended by road traffic activity, and sea spray. All of these sources are dependent in some way upon meteorology (strength of wind, dryness of soil etc) and their influence may in some instances be a rather local one, especially as particle sizes tend to be quite large and hence atmospheric lifetime rather limited. Emissions inventories of particulate matter in the United States have sought to include wind blown soil and resuspended road dust but the results obtained have not been regarded with high credibility and the methodology is currently being revised. The data used to derive emissions estimates from these sources have come largely from dry climates where the importance of such sources is greater and extrapolation to the wetter United Kingdom climate is problematic.

Source inventories thus describe rather well emissions from fuel combustion and industry, as exemplified by the inventories contained in Chapter 4. A different approach is however needed in order to quantify secondary sources of PM_{10} and the sources such as road dust, marine aerosol and particles generated from building and demolition activity for which the inventories cannot give good estimates. Currently the best available approach to quantifying these sources is through a range of procedures known generically as receptor modelling. Such techniques use as a starting point measurements of particulate matter and its individual components within the atmosphere. In conjunction with gaseous pollutant and meteorological data, these measurements are used to infer the contributions of different source types to atmospheric concentrations. This chapter seeks to introduce the techniques which have been applied in the UK atmosphere and to present resultant data.

8.2 RECEPTOR MODELLING OF TOTAL SUSPENDED PARTICULATE MATTER

Two main types of technique have been reported in the research literature for source apportioning the total mass of particulate matter in the atmosphere. The chemical mass balance method requires a knowledge of both the concentrations of various chemical components of the ambient aerosol, and their fractions in source emissions. A complete knowledge of the composition of emissions from all contributing sources is needed and these are combined in varying proportions in such a way as to optimally account for the composition of particles in the atmosphere. This method assumes *a priori* that certain classes of sources are responsible for ambient concentrations of elements measured at the receptor. Furthermore it is assumed that each source under consideration emits a characteristic and conservative set of elements (Friedlander, 1973). Whilst the chemical mass balance approach can cope reasonably well with primary emissions if the local source characteristics are well understood, its ability to cope with a complex urban atmosphere and with secondary aerosol is very poor. Such methods have not been applied to the comprehensive apportionment of aerosol in the UK atmosphere.

The second type of approach to source apportionment uses one or more of the multivariate methods which extract information about the contribution of a source on the basis of the variability of chemical components measured in a large number of atmospheric samples. If two or more chemical components originate from the same source, their variability as a function of time as measured at a receptor will be similar. The objective of multivariate methods is to detect this common variability after the fact and infer source identity by comparing the elements with common variability to the elements associated with specific sources (Alpert and Hopke, 1981). In contrast to the chemical mass balance method, no quantitative chemical composition data for source emissions are required to determine the contributions of various source types as the contributions are estimated solely on the basis of statistical analysis of ambient air data. The disadvantages of this approach are that large numbers of ambient samples must be collected and measured and that statistically independent source tracers are required for each major source type. Also, it has been observed (Henry et al, 1984) that in practice multivariate techniques can only usually identify between five and eight source categories. Typical marker species have been identified as follows (Gordon, 1988); oil burning (V, S, Ni); marine (Na, Cl); refuse burning (Zn, Cu); soil (Mn, Fe, Ti); coal (As, Se); vehicular (Pb, Br, elemental carbon); secondary aerosol (SO_4, NO_3, NH_4); metallurgical (Fe, Mn, Cr).

A receptor modelling study of the total suspended particulate matter sampled in Edgbaston, Birmingham has been carried out by Smith and Harrison (1995). Analytical data was collected on 24-hour airborne particle samples for a range of trace elements, ions and organic components. Meteorological data was collected simultaneously. Sampling took place over one month in the Summer of 1992 and one month during the following Winter. The multivariate method employed was Principal Component Analysis followed by Multi-Linear Regression Analysis. Source categories for aerosol constituents were identified by means of Principal Component Analysis performed using the orthogonal transformation method with Varimax rotation and retention of principal components whose eigenvalues were greater than unity (Pio, 1991; Thurston, 1983). This method allows the identification of source categories. The contribution of each such source category to the aerosol burden was then quantitatively assessed for each data set by means of Multi-Linear Regression Analysis which was applied using trace element and compound concentrations as dependent variables and absolute factor scores obtained from Principal Component Analysis as independent variables. The data was analysed in a number of separate combinations of Winter and Summer data and coarse and fine data and different chemical and meteorological components. Table 8.1 shows the factor loadings obtained from the Principal Component Analysis using as input data fine fraction trace elements and anions, polynuclear aromatic hydrocarbons (sum of particulate and gas phase) and meteorological data. The higher the factor loading the greater the association of that chemical component or meteorological variable with the individual factor. A negative value indicates that a variable is anticorrelated with the factor. Six factors are identified by the Principal Component Analysis which have been tentatively associated with different source categories indicated at the base of the table. All of the source categories for the Birmingham data have distinct characteristics and have been assigned on the basis of relevant marker species.

Factors 1 and 4

The direct vehicular source (factor 4) can be identified by high loadings on lead, bromine and elemental carbon. Factor 1 also contains lead and bromine, but with a higher contribution of other elements suggesting contaminated road dust. High loadings on iron and manganese are suggestive of crustal material such as soil which is know to be the bulk matrix of road dust although there are also minor emissions of iron from road vehicles. Frequently Principal Component Analysis does not well separate road dust from vehicular emissions and there does seem to be some overlap in this dataset.

Factor 2

High loadings for sulphate, nitrate and ammonium indicate secondary aerosol. Most of the percentage contribution to vanadium and sulphur appears in this factor providing evidence for oil combustion.

Factor 3

The combustion of coal can be established through two key markers of selenium (measured, but not reported here) and arsenic. A contribution of potassium and elemental carbon is also to be expected.

Factor 5

Incineration is normally associated with high loadings of copper and zinc as in this instance, and commonly accompanied by moderate loadings for fine size fractions of sodium and chloride.

Table 8.1 Factor Loadings obtained from Principal Component Analysis of Urban TSP Composition Data from Birmingham (Smith and Harrison, 1995).

Species	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**	**Factor 6**
S	0.515	0.575	0.435			
Cl						0.780
K			0.792			
V	0.615	0.439				
Mn	0.621			0.629		
Fe	0.541	0.280		0.564	0.372	
Ni			0.797			
Cu					0.842	
Zn					0.913	
As			0.684			
Br	0.371			0.637		
Pb	0.387			0.746	0.391	
Na	0.435				0.424	0.420
NH_4		0.913				
NO_3		0.741				
SO_4		0.833	0.308			
Elem C		0.254	0.286	0.796		
Fluorene	0.704	0.319			0.529	
Phenanthrene	0.714	0.380		0.268	0.253	0.255
Fluoranthene						0.780
Pyrene	0.746	0.431			0.253	0.251
Chrysene	0.736	0.275	0.324	0.257		
Benzo(b)fluoranthene	0.755	0.257				
Benzo(k)fluoranthene	0.848		0.247			
Benzo(a)pyrene	0.926					
Benzo(g,h,i)perylene	0.873			0.340		
Indeno[1,2,3,c-d]pyrene	0.552	0.513				
Coronene	0.716			0.492		
BNT	0.721		0.245	0.353		
TSP	0.597	0.360			0.424	
Temperature	- 0.615	- 0.273	- 0.391		- 0.423	- 0.236
Relative Humidity		0.522				0.497
Precipitation						
Solar Radiation		- 0.375				- 0.440
Wind Velocity		- 0.340	0.629	- 0.357		0.278
INFERRED SOURCE	**road dust**	**secondary and oil**	**coal**	**vehicular**	**incineration**	**road salt**

Factor 6

Sodium and chloride are easily recognised as marine emissions or re-suspended road salt.

Multi-Linear Regression Analysis has been used to provide quantitative estimates of the percentage contribution of each source category to the various chemical components measured and to total suspended particulate matter. The results are shown in Table 8.2. Also included in Table 8.2 are the multiple correlation coefficients, r, which indicate that the factors elucidated account for a large percentage of the variance in the measured concentration data. It must be emphasised that at present multivariate methods are still under development and cannot be assumed to provide accurate quantitative information

Table 8.2 Percentage Contribution of each Inferred Source to Total Concentration of each TSP Component and Multiple Correlation Coefficients (r) (from Smith and Harrison, 1995).

Species	Constant	Road Dust	Secondary and Oil	Coal	Vehicular	Incineration	Road Salt	r
S	-	19 ± 6	48 ± 4	25 ± 5	3 ± 5	1 ± 3	4 ± 6	0.96
Cl	-	-5 ± 5	-3 ± 2	12 ± 3	22 ± 10	14 ±4	60 ± 3	0.92
K	-	39 ± 6	-1 ± 1	44 ± 18	4 ± 1	12 ± 7	2 ± 4	0.96
V	-	39 ± 8	45 ± 5	5 ± 1	-2 ± 3	16 ± 9	-3 ± 1	0.92
Mn	8 ± 2	50 ± 6	3 ± 1	-1 ± 1	36 ± 6	9 ± 1	-5 ± 2	0.95
Fe	8 ± 4	34 ± 10	8 ± 3	10 ± 5	24 ± 4	12 ± 2	4 ± 3	0.93
Ni	15 ± 2	10 ± 2	22 ± 2	32 ± 6	7 ± 2	16 ± 1	-2 ± 1	0.94
Cu	6 ± 2	21 ± 9	11 ± 1	-1 ± 1	6 ± 4	59 ± 10	-1 ± 3	0.82
Zn	-	12 ± 5	-4 ± 5	14 ± 4	6 ± 2	74 ± 8	-2 ± 4	0.88
As	-	14 ± 4	1 ± 2	84 ± 9	0 ± 2	1 ± 2	0 ± 1	0.88
Br	2 ± 5	27 ± 7	9 ± 5	1 ± 1	55 ± 8	5 ± 2	1 ± 1	0.97
Pb	3 ± 3	22 ± 9	-3 ± 4	5 ± 3	60 ± 16	12 ± 3	1 ± 2	0.97
Na	-	6 ± 4	-3 ± 3	10 ± 5	3 ± 1	23 ± 6	61 ± 5	0.84
NH_4	2 ± 1	20 ± 8	74 ± 8	2 ± 2	3 ± 5	-1 ± 1	-1 ± 1	0.94
NO_3	-	25 ± 8	68 ± 5	-1 ± 1	7 ± 2	-2 ± 1	3 ± 2	0.80
SO_4	-	6 ± 1	65 ± 7	16 ± 4	12 ± 8	0 ± 2	1 ± 3	0.93
Elem C	4 ± 5	2 ± 3	11 ± 6	22 ± 11	54 ± 4	5 ± 1	2 ± 2	0.94
Fluorene	5 ± 2	40 ± 10	14 ± 5	4 ± 1	7 ± 2	20 ± 6	8 ± 1	0.88
Phenanthrene	-	33 ± 2	26 ± 5	-3 ± 1	15 ± 7	16 ± 3	13 ± 2	0.98
Fluoranthene	-	35 ± 4	23 ± 3	0 ± 1	12 ± 5	10 ± 2	20 ± 6	0.98
Pyrene	-	36 ± 5	33 ± 3	-5 ± 2	8 ± 4	18 ± 3	10 ± 3	0.97
Chrysene	9 ± 2	35 ± 3	18 ± 4	22 ± 12	15 ± 8	2 ± 1	-1 ± 1	0.93
Benzo(b)fluoranthene	-	69 ± 6	20 ± 7	-1 ± 1	12 ± 5	-2 ± 2	1 ± 2	0.95
Benzo(k)fluoranthene	-	61 ± 3	8 ± 3	19 ± 4	10 ± 1	3 ± 1	-1 ± 3	0.95
Benzo(a)pyrene	-	65 ± 4	3 ± 1	5 ± 2	23 ± 8	7 ± 5	-3 ± 5	0.98
Benzo(g,h,i)perylene	7 ± 5	58 ± 20	-1 ± 3	4 ± 1	28 ± 18	-2 ± 1	6 ± 7	0.88
Indeno[1,2,3,c-d]pyrene	2 ± 6	53 ± 12	22 ± 13	1 ± 1	18 ± 5	4 ± 5	0 ± 1	0.99
Coronene	-	61 ± 12	8 ± 5	1 ± 2	32 ± 7	-1 ± 1	-1 ± 2	0.94
BNT	7 ± 6	29 ± 8	7 ± 5	14 ± 3	41 ± 10	2 ± 2	0 ± 2	0.96
TSP	-	32 ± 5	23 ± 4	11 ± 7	25 ± 8	7 ± 2	2 ± 2	0.92

Note: BNT = Benzo(b)naphtho[2,1-d]thiophene

upon source contributions. Their value is in highlighting likely source categories and giving some feel for their relative importance. Thus in the context of total suspended particulate matter (which includes some particulate material larger than PM_{10}), the most important sources are indicated as road traffic exhaust, road dust and secondary aerosol. This is highly consistent with the other data presented in this chapter.

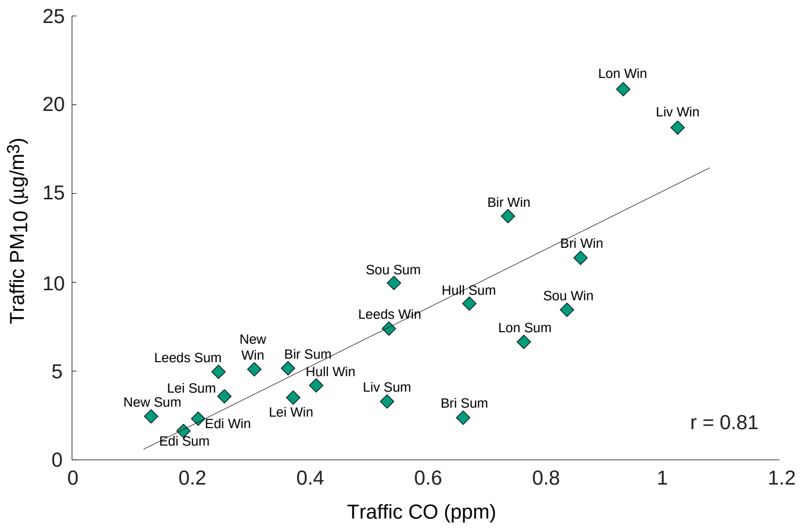
8.3 RECEPTOR MODELLING AND SOURCE APPORTIONMENT OF PM_{10}

To date, no detailed multi-element receptor modelling study of the type described above has been carried out in the UK for PM_{10}. There is, however, a rich base of data on hourly average PM_{10} concentrations from the Automatic Urban Network sites as well as simultaneous data for other pollutants. These data have been utilised to estimate the road traffic contribution to PM_{10} within UK urban areas.

According to the available emission inventories, 91% of carbon monoxide nationally and 98% in London arises from motor traffic. Carbon monoxide therefore provides an excellent tracer for traffic emissions and this fact can be used to estimate the quantity of PM_{10} in city air arising from this source. The technique used involves splitting the air monitoring data into four seasons, and within each season extracting data for carbon monoxide and PM_{10} for twelve alternate hours of the day. For any given hour, eg 12 noon, the paired data for carbon monoxide and PM_{10} for a given site at that time on each day in the appropriate season of the year are pooled and the relationship between the carbon monoxide and PM_{10} concentration calculated using linear regression analysis. In summer and winter particularly, the correlations between the two pollutants are highly significant allowing a relationship to be identified with some confidence. Although virtually all emissions of carbon monoxide within an urban area arise from road traffic, there is an external background contribution to the urban concentration. The northern hemisphere background of carbon monoxide arises from a number of sources and has of magnitude of about 0.125 ppm (Novelli et al, 1994). Derwent et al (1994) using measurements from the Atlantic coast of Ireland have shown a seasonal dependence of background carbon monoxide, with in recent years background concentrations averaging 0.10 ppm in summer and 0.14 ppm in winter. The regression equation between carbon monoxide and PM_{10} was used to estimate the PM_{10} concentration corresponding to the appropriate seasonal background of carbon monoxide and hence to a situation with zero influence of local motor traffic. The concentration of PM_{10} thus arrived at corresponds to the PM_{10} in air which does not arise from road traffic. Subtraction of this concentration from the measured average concentration for the site and season gives an estimate of the concentration of PM_{10} generated from road traffic. Such a calculation has been performed for each alternate hour of the day at the ten Automatic Urban Network sites with the longest run of data for separate seasons of the year.

Figure 8.1 shows the calculated PM_{10} arising from traffic, related to the carbon monoxide estimated due to traffic. There is a point for the summer and winter season data for each of the sites. Thus, over the ten urban areas as a whole, traffic-generated PM_{10} is quite strongly correlated with traffic-generated carbon monoxide, with a correlation coefficient of 0.81. The gradient of the line corresponds to the ratio of traffic-generated carbon monoxide to traffic-generated PM_{10}. When the concentrations of the two pollutants are converted to the same units, the gradient of the line corresponding with the ratio of CO to PM_{10} is equal to 82.8. This may be compared with the traffic-derived ratio of carbon monoxide to PM_{10} emissions in the national and London inventories which show respectively ratios of 78 (national, 1993); 94 (Greater

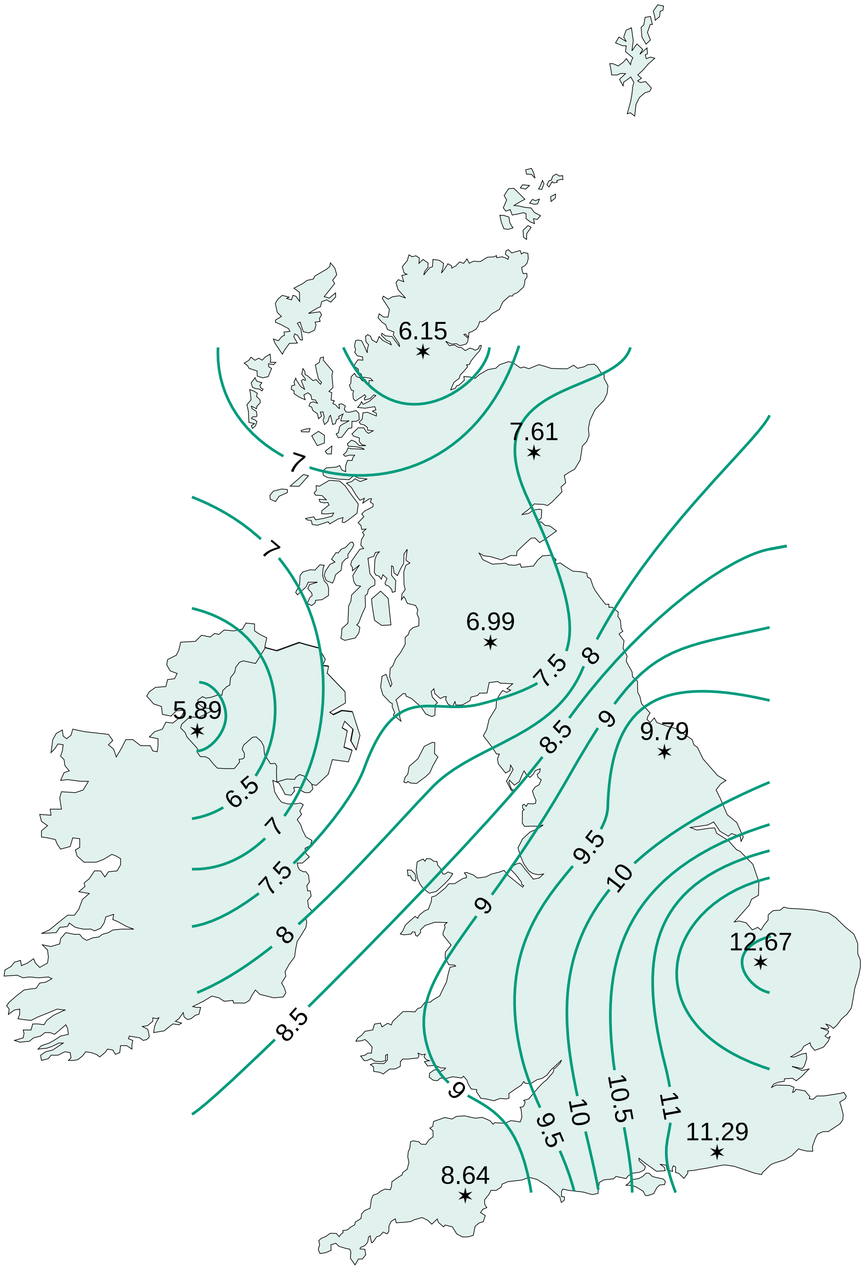
Figure 8.1 Traffic Contribution to CO and PM10 in 10 UK Cities.



London, 1990) and 84 (City of London, 1990). The closeness of this agreement with the inventory ratios is very encouraging, and the fact that the ratio derived from receptor modelling lies between the national and London inventory values probably reflects the fact that urban traffic in cities other than London has a composition and speed somewhere between that of the country as a whole, including rural areas and motorways, and London where the pattern of traffic is very different.

The other major component of PM_{10} in the UK is the secondary aerosol component comprising sulphates and nitrates from atmospheric oxidation of sulphur and nitrogen oxides. This has been estimated by using measurement data collected for EMEP (the European Measurement and Evaluation Programme). EMEP

Figure 8.2 Interpolated Long-term Average Concentration of Secondary Particulate Matter across the UK (µg/m^3).

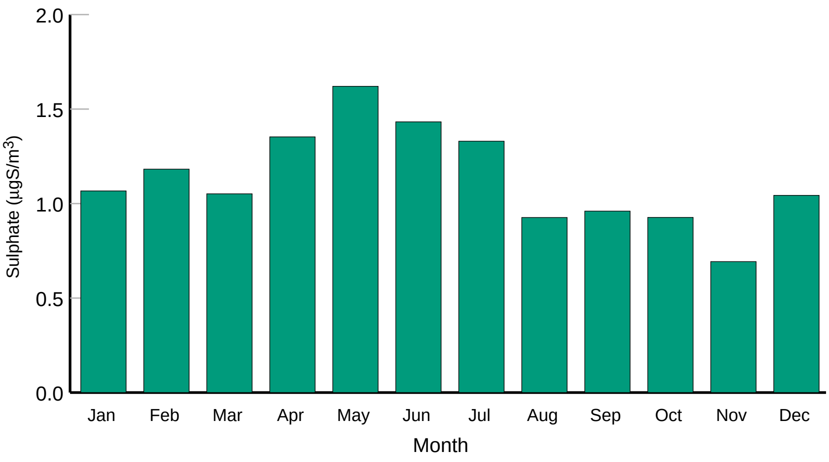


sulphate data have been converted to an equivalent weight of ammonium sulphate, and the EMEP nitrate data, which reflect the sum of nitrate particles and nitric acid vapour, have been adjusted to subtract the nitric acid vapour component (assumed to be 12.3% based on measurement data from Allen and Harrison (1990)) and subsequently converted to an equivalent mass of ammonium nitrate. Data from some eight sites across the country are available for sulphate allowing the distribution to be mapped. Unfortunately for nitrate, data are available from only two sites, and the distribution of nitrate across the UK has been assumed to be similar to that for sulphate. The result of mapping the total secondary particulate is shown in Figure 8.2. It may be seen that the highest concentrations of secondary particles are in East Anglia with concentrations generally diminishing towards the north and west of the UK This is consistent with the result of two influences. The first is that emissions of nitrogen and sulphur oxides in the west of the UK require time to be converted to secondary aerosol as the prevailing south-westerly winds carry them across the United Kingdom; this results in higher levels to the east. The other influence is that of continental sources of secondary aerosol, which is carried to the UK during long range transport and thus has its greatest effect in the east of the UK, being closest to the European continent. The sulphate data averaged across all UK sites show a seasonal cycle (Figure 8.3) with highest concentrations in Spring and Summer.

Using Figure 8.2, an annual average secondary particle contribution to PM_{10} has been established for each of the urban sites for which traffic-related PM_{10} has been calculated. The sum of vehicular (estimated by the PM_{10}-CO correlation method above) and secondary PM_{10} account for a high percentage of total PM_{10}. The remaining PM_{10} unaccounted for by this method arises from other sources such as wind-blown soil, construction work, industrial emissions and marine particles. Barbecues and bonfires also contribute on an occasional basis. It should be noted that the resuspended street dust and soil indicated as an important source from the receptor modelling of total suspended particulate matter is not accounted for in the vehicular PM_{10} estimated by this method as it is only the exhaust-emitted PM_{10} which correlates with carbon monoxide. Additionally, it should be recognised that the calculated vehicular PM_{10} is only the primary emitted particles, and that secondary nitrate particles arising from oxidation of oxides of nitrogen emitted from vehicles is included as secondary rather than vehicular PM_{10}. Nitrate accounts for on a national average basis about 3.9 µg/m³ of PM_{10}. Since 49% of national NO_x emissions arise from road transport, about 2 µg/m³ of nitrate particles, or 8% of typical urban PM_{10} may be attributed to the vehicular source.

In a further analysis of data from 1993, months were selected in which good correlations ($r > 0.5$) of CO with PM_{10} were observed. In all, 64 months out of a

Figure 8.3 **Monthly Mean Sulphate Concentration, 1990-1992 EMEP Data (all sites).**



total of 168 met this criterion; of these, 61 were in the cooler months of the year, September to April. Rather than aggregating the data by hour of the day, the measurements were then analysed as daily subsets. Only those days were processed for which five or more hourly values were available for both pollutants. For those days with a well-defined regression equation, an estimate of PM_{10} at background CO was made, and the traffic-related PM_{10} determined by difference from the daily mean. Table 8.3 summarises the estimated "traffic-related" fractions for all sites and days for which the linear regression equations were well-defined. Clearly, there are wide distributions in these fractions over all the sites during 1993. The mean "traffic-related" fractions vary from 0.66 at Edinburgh to 0.79 at London Bloomsbury. These fractions cover a substantial number of days per year at each site, which vary from 160 at Edinburgh to 223 in Belfast, during 1993. When days with mean PM_{10} concentrations above 50 µg/m^3 and those with well-defined correlations are selected, then the "traffic-related" fractions increase somewhat though the number of days meeting this stricter criterion falls sharply. The mean "traffic-related" fractions then vary from 0.68 at Edinburgh to 0.84 at Belfast. The frequency of days with low "traffic-related" fractions, that is with ratios less than 0.4, falls to zero. These data include values for Belfast, where combustion of solid fuels within homes leads to emissions of both PM_{10} and CO, thus enhancing the apparent PM_{10} due to road traffic. Further studies which have used NO_x as the tracer of road traffic have indicated very similar

TABLE 8.3 Summary of the Fraction of the PM_{10} at Each Site During 1993 which is "Traffic-Related", Based on Daily Linear Regression Analyses of Hourly PM_{10} and Carbon Monoxide Concentrations.

Site	Number of days with r>0.5	Fraction of PM_{10} which is "Traffic-Related" on days with r>0.5	Fraction of PM_{10} which is "Traffic-Related" on days with r>0.5 and PM_{10}>50 µg/m^3
Belfast	223	0.75	0.84
Birmingham	175	0.76	0.80
Bristol	181	0.76	0.79
Edinburgh	160	0.66	0.68
Leeds	204	0.74	0.80
Liverpool	133	0.78	0.80
London, Bloomsbury	190	0.79	0.83
Newcastle	193	0.69	0.75

Site	Number of days with fraction	<0.6	0.6-0.7	0.7-0.8	0.8-0.9	0.9-1.0
Belfast		34	39	66	63	21
Birmingham		8	34	67	56	9
Bristol		15	22	72	56	16
Edinburgh		47	46	55	12	0
Leeds		22	45	76	58	3
Liverpool		13	12	26	72	10
London Bloomsbury		9	17	57	89	19
Newcastle		32	58	76	26	1

Notes:

a. Linear regressions were performed on each days hourly data for PM_{10} and CO and those days were selected in which the regression equation was well-defined, r>0.5. Based on provisional data.

b. The "baseline" PM_{10} contribution was defined from the daily regression equation at [CO]=0.12 ppm and the "traffic-related" contribution obtained by subtracting this figure from the daily mean PM_{10} concentration.

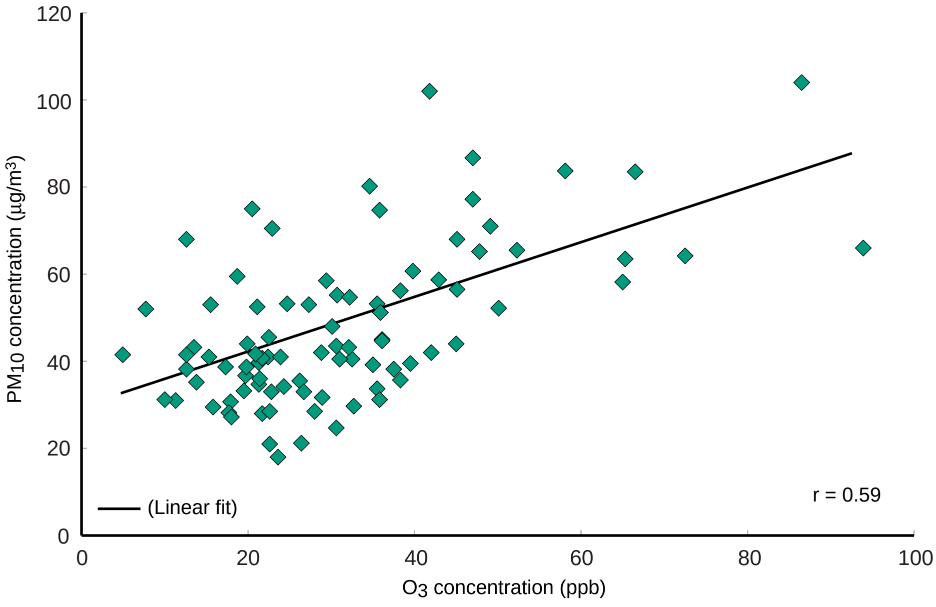
contributions to PM_{10}. The use only of days with high correlation coefficients leads to a high confidence in the result for those days, but tends to select the days when the traffic contribution of PM_{10} is highest. The data in Figure 8.1 include all days within three month summer and winter periods and, although less precise, may be more representative. Overall, it appears that in Winter about 40-50% of PM_{10} arises from vehicle exhaust emissions, with a higher percentage on days with elevated PM_{10}. Additionally, it should be noted that vehicle emissions account for a larger proportion of the more health-related $PM_{2.5}$ fraction.

A similar analysis of summer data shows generally poorer correlations of PM_{10} with CO and NO_x and indicates that for most sites the summer contribution of road traffic to PM_{10} is appreciably less than in the winter months. This is interpreted as resulting from improved vertical mixing of pollutants in the Summer and is consistent with general seasonal behaviour of primary pollutants. In summer, high episodic concentrations of secondary particles may contribute to elevated levels of PM_{10}. The formation of secondary particles is favoured by the atmospheric conditions which lead to high ozone, and the two pollutants tend to correlate. Thus in Figure 8.4 the maximum hourly ozone in each day is plotted against the highest hourly PM_{10}, confirming that the secondary aerosol tends to be elevated during Summer photochemical pollution events.

Taking maximum hourly PM_{10} concentrations in Figure 8.4 of >60 µg/m^3, maximum hourly ozone exceeds 40 ppb on 14 out of 19 occasions, suggesting that secondary PM_{10} is responsible for the majority of episodes of high PM_{10} in the Summer months. A detailed analysis of sulphate and nitrate data would be required to better quantify this effect, but has not been conducted as the necessary 24-hour data are not available. The tendency for summer weather conditions simultaneously to promote dispersion of primary pollutants and formation of secondary particles leads to the much poorer relationships observed between PM_{10} and other traffic-related pollutants observed in summer than in winter, as noted at other points in this report. In winter ozone is usually negatively correlated with PM_{10} as traffic generated NO_x leads to net ozone destruction in urban areas in the winter months.

Further insights into the ratio of carbon monoxide to PM_{10} in road traffic emissions can be gained from analysis of short-lived peaks during winter episodes, an example of which is shown in Figure 8.5. Using

Figure 8.4 **Daily Maximum Hourly-Average Ozone versus Peak Hourly Average PM_{10} at London (Bloomsbury), Summer 1994.**



the data from the peaks on the night of 23/24 December at the Birmigham (Centre) AUN site, the ratio of CO to PM_{10} was between 52 and 96 (mean 81), highly consistent with the road traffic ratio from the inventories showing that the peaks after subtraction of background were almost 100% generated from road traffic emissions. A very different case is illustrated by Figure 8.6 which shows a summer ozone episode at the London Bloomsbury AUN site. It may be seen that when ozone concentrations approached 100 ppb there was a steady increase in PM_{10} consistent with photochemical

Figure 8.5 Time Series of Hourly PM_{10} and CO in Birmingham, 23-25 December 1992.

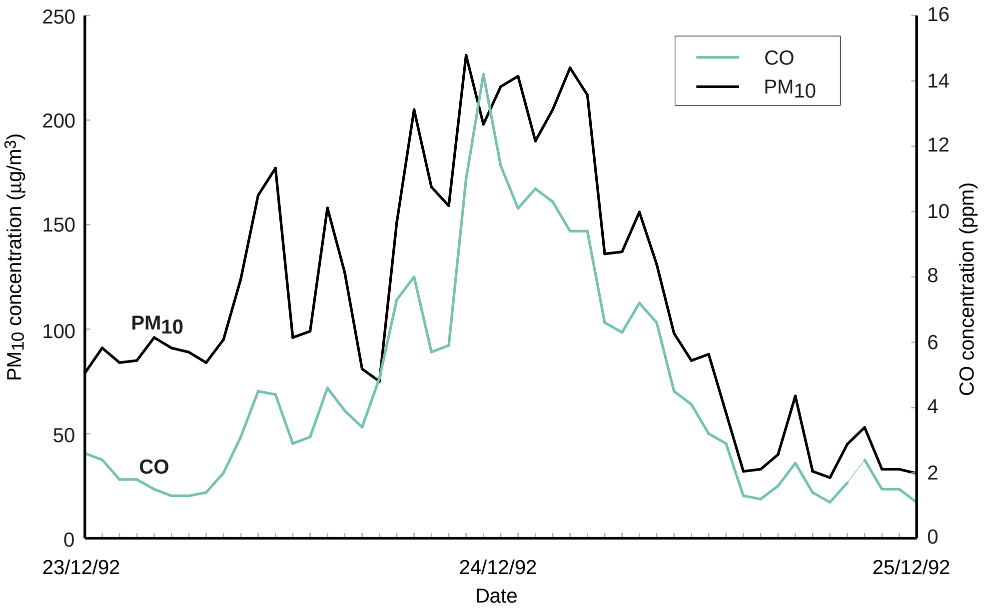
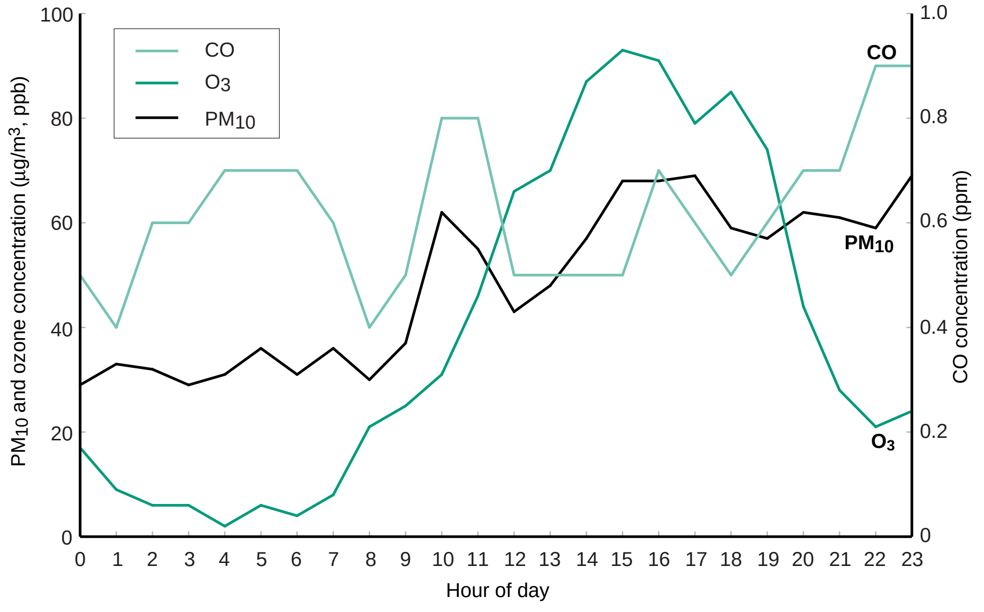


Figure 8.6 Time Series of Hourly PM_{10}, CO and Ozone in London, 6 June 1993.



formation. After subtraction of northern hemisphere background CO, the CO to PM_{10} ratio is 15.5 suggesting that less than 20% of PM_{10} in this instance is from primary road traffic emissions.

8.4 INTERPRETATION OF PM_{10} AND $PM_{2.5}$ DATASET FROM NORTH-WEST BIRMINGHAM

A site in North-West Birmingham (Birmingham, Hodge Hill) some 70 metres from the elevated section of the M6 motorway (see Figure 8.7) has been used for simultaneous automated sampling of PM_{10} and $PM_{2.5}$ particles using TEOM instruments. The data collected between October 1994 and March 1995 have been analysed.

The mean concentration at PM_{10} at the site over this period was 16.5 µg/m³, somewhat lower than at the Birmingham Central (22.3 µg/m³) and Birmingham East (21.4 µg/m³) stations of the Automatic Urban Network. The site is clearly traffic influenced as evidenced by the concentration of NO_x, which at 60.9 ppb is higher than either Birmingham Central or Birmingham East, (56.0 ppb and 52.0 ppb respectively). At this site, both PM_{10} and $PM_{2.5}$ correlate strongly with hourly NO_x. The regression equations are as follows:

$$PM_{2.5}\ (\mu g/m^3) = 0.114\ NO_x\ (ppb) + 6.54 \qquad r = 0.70$$

$$PM_{10}\ (\mu g/m^3) = 0.134\ NO_x\ (ppb) + 11.31 \qquad r = 0.70$$

If the NO_x is taken to be wholly traffic-related, which will be a reasonable assumption at this site as the location is in a heavily trafficked area of a major conurbation, then there is a background of PM_{10} of 11.3 µg/m³ upon which a mean traffic-related concentration of PM_{10} of 5.2 µg/m³ is superimposed. Similarly, for $PM_{2.5}$ the background is 6.5 µg/m³ with a mean concentration of 4.5 µg/m³ of traffic-related particles.

The coarse particle mass can be calculated for each individual hour from the difference between PM_{10} and $PM_{2.5}$. Its mean concentration is 5.5 µg/m³. Coarse particle mass is poorly correlated with NO_x,

$$PMcoarse\ (\mu g/m^3) = 0.018\ NO_x\ (ppb) + 5.3 \qquad r = 0.33$$

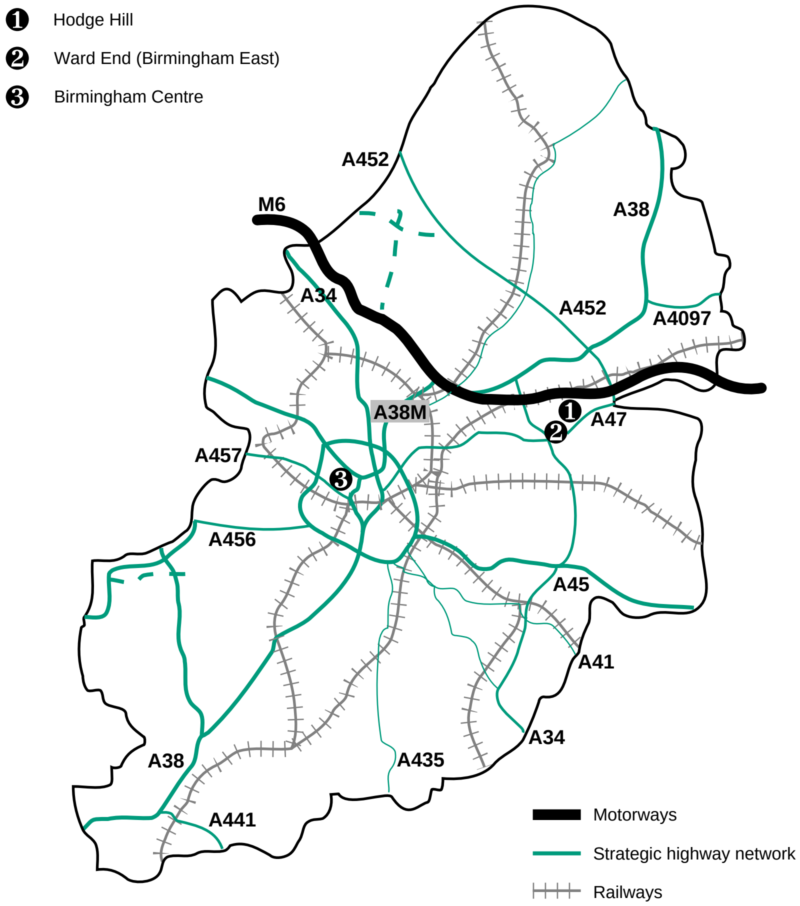
Based on the above regression equations, road traffic is on average responsible for 41% of $PM_{2.5}$ mass, 32% of PM_{10} mass and 3% of coarse particle mass. This is highly consistent with size distribution measurements of vehicle exhaust which show primary traffic-emitted particles to be very small in size and thus predominantly in the $PM_{2.5}$ fraction. The contribution of road traffic to coarse particles is, as expected, very small.

The correlation of $PM_{2.5}$ with NO_x indicates that on average 4.5 µg/m³ arises from road traffic and 6.5 µg/m³ comes from other sources. The mean annual average concentration of secondary sulphate and nitrates predicted for Birmingham from the map in Figure 8.2 is 10 µg/m³. Approximately 80% of sulphate and nitrate mass is expected to be in the $PM_{2.5}$ fraction, and applying a seasonal adjustment (Figure 8.3), this translates to a secondary $PM_{2.5}$ contribution over the months October to March of 7.0 µg/m³, almost identical to the non-traffic related $PM_{2.5}$ of 6.5 µg/m³. It may thus be concluded that $PM_{2.5}$ is accounted for almost wholly by traffic exhaust-emitted and secondary particles. On the other hand, coarse particles, which account for approximately one third of the PM_{10} mass in this case, are not associated with vehicle exhaust emissions, although they may arise in part from wear of tyres and road surfaces and resuspension of dust by passing traffic.

8.5 IMPLICATIONS FOR THE CONTROL OF ATMOSPHERIC CONCENTRATIONS OF PM_{10}

Figure 8.8 shows hourly concentrations of coarse particles as a function of PM_{10} concentrations. If we define elevated concentrations of PM_{10} as above 50 µg/m³, then there are five hours in which coarse particles make the major contribution to raised levels of PM_{10}. For the other 150 hours of elevated PM_{10}, whilst the PM_{10} concentration increases to 170 µg/m³, the coarse particle mass is almost level at around 20-25 µg/m³. Thus by far the majority of episodes (97% in this dataset) are those associated with excursions in

Figure 8.7 Locations of Air Quality Sampling Sites in Birmingham.



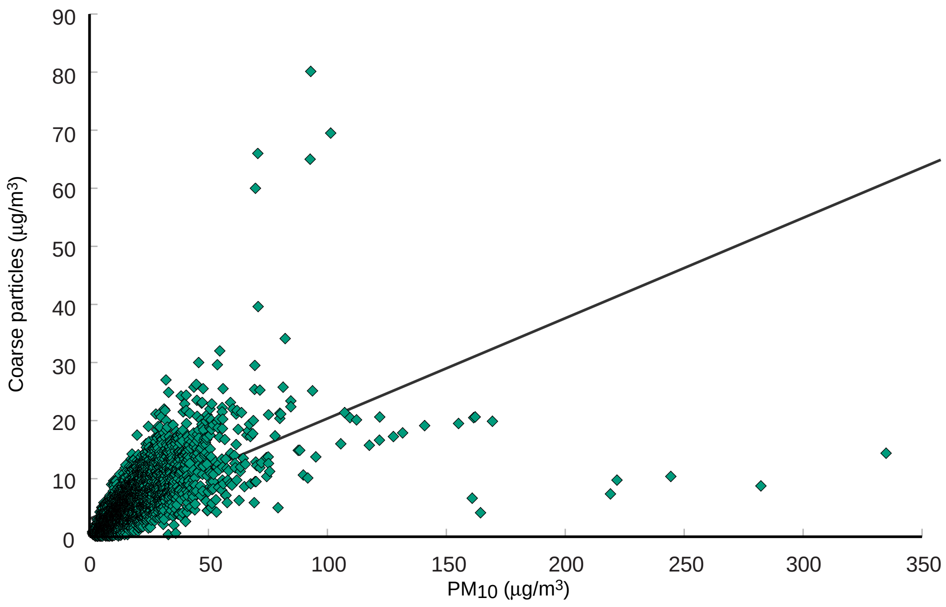
Source: Adapted from Birmingham City Council - The Environment in Birmingham: 1993.

$PM_{2.5}$ concentrations. *Thus, if elevated concentrations of PM_{10} are to be avoided in the Winter (when most episodes occur), the primary requirement will be control of the sources of $PM_{2.5}$.*

As noted above, the main sources of $PM_{2.5}$ are (a) road transport emissions and (b) secondary aerosol. A clear indication of the relative importance of these two sources at the Birmingham, Hodge Hill site in the winter of 1994-95 may be gained from Figures 8.9 and 8.10 which relate PM_{10} and $PM_{2.5}$ to NO_x, itself a good indicator of local vehicle emissions. There is a group of some seven points where at concentrations of NO_x below 250 ppb, the concentration of particulate matter exceeds 150 µg/m³. These are episodes where substantially elevated $PM_{2.5}$ is not associated with NO_x and these are interpreted as due to a local source, probably industrial in character. For the remaining data, $PM_{2.5}$ generally relates closely to NO_x. There are a few points where $PM_{2.5}$ exceeds 50 µg/m³ which lie well above the regression line and these are interpreted as having a major contribution from secondary particles. The vast majority of points, however, lie very close to the regression line indicating that road traffic is far the major cause of elevated $PM_{2.5}$, and by implication of PM_{10}, at this site. It should be noted that this is not an abnormally polluted site since it has PM_{10} concentrations lower than Birmingham Central and Birmingham East, and a mean NO_x concentration only slightly higher.

The very clear implication of this dataset is that in the winter period the control of elevated concentrations of PM_{10} can only be achieved by reduction of road traffic emissions. Thus, whilst control of SO_2 and NO_x emissions will have a benefit upon concentrations of

Figure 8.8 **Plot of Hourly Coarse Particles versus PM_{10} for Birmingham, Hodge Hill; October 1994 to March 1995.**



secondary $PM_{2.5}$ and PM_{10} as indicated in Chapter 5, this will not have any substantial influence upon winter episodes of PM_{10} pollution.

8.6 SUMMER DATA

Data from the months April to July 1995 have been analysed by the same methods as for the winter data.

In the summer period, the mean PM_{10} at the Hodge Hill site was 24.7 µg/m³, the same as at Birmingham Centre (24.7 µg/m³) and higher than at Birmingham East (18.3 µg/m³). However, the maximum hourly PM_{10} was highest at Birmingham Centre (193 µg/m³), followed by Birmingham East (137 µg/m³) and Hodge Hill (118 µg/m³). Mean NO_x was highest at Hodge Hill (49.1 ppb) compared with Birmingham Central (31.5 ppb) and Birmingham East (22.5 ppb).

The mean concentration of $PM_{2.5}$ at Hodge Hill was 13.1 µg/m³, representing only 53% of PM_{10}. The two were quite strongly correlated:

$$PM_{2.5} = 0.51\ PM_{10} + 0.57\ (\mu g/m^3) \qquad r = 0.85$$

Correlations of PM_{10} and $PM_{2.5}$ with NO_x were positive, but weak in comparison with the winter data.

Figures 8.11 and 8.12 show the relationship between fine ($PM_{2.5}$) and coarse (PM_{10} minus $PM_{2.5}$) particles respectively and PM_{10}. The data show broad scatter across an envelope with outer bounds of around 85% coarse particles at one extreme and 85% fine at the other extreme. The high abundance of coarse particles, which exceeds that found in other studies in Birmingham, is probably associated with the unusually dry weather over much of this period. Concentrations of hourly PM_{10} above 50 µg/m³ are associated both with coarse and fine particles. Exceedences of 90 µg/m³ are in all but one instance associated with a predominance of $PM_{2.5}$ and the implications for control of excursions are the same as for the winter period, with the caveat that occasionally episodes of coarse dust may be a problem.

8.7 MEETING THE EPAQS RECOMMENDED STANDARD

Table 6.17 lists exceedences of various thresholds in 24 hour average concentration of PM_{10}. There are currently many exceedences of 50 µg/m³ over 24 hours, but far fewer exceedences of 100 µg/m³ and virtually none of 150 µg/m³. Exceedences of the 50 µg/m³ threshold are more frequent for the rolling 24-hour mean than the fixed (midnight to midnight)

Figure 8.9 **Plot of Hourly Fine Particles ($PM_{2.5}$) versus NO_x for Birmingham, Hodge Hill; October 1994 to March 1995.**

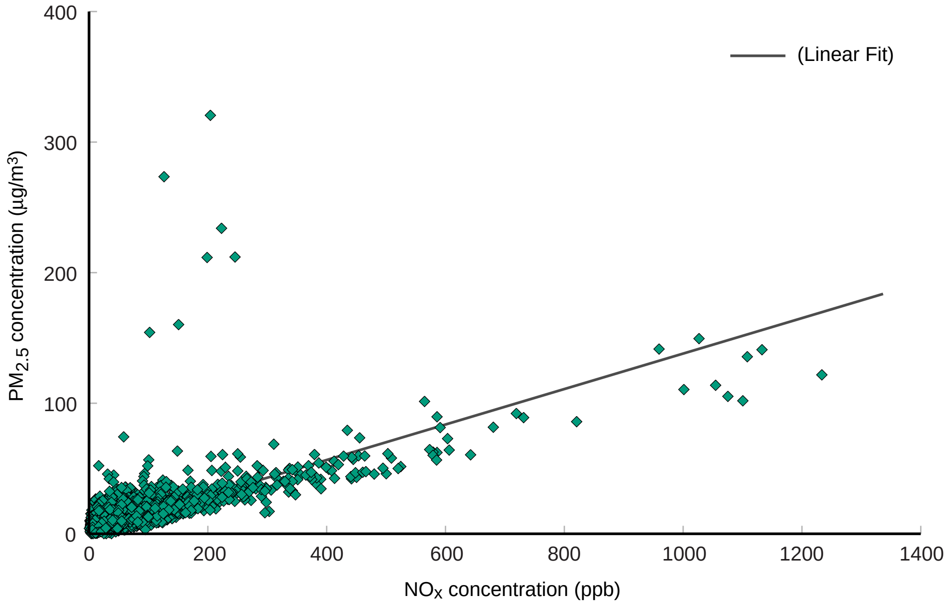
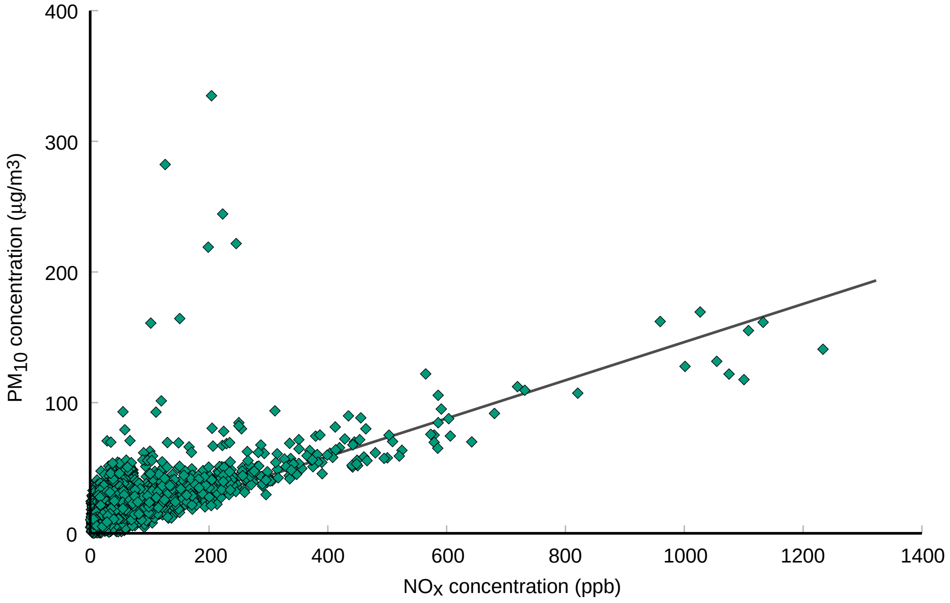


Figure 8.10 **Plot of Hourly PM_{10} versus NO_x for Birmingham, Hodge Hill; October 1994 to March 1995.**



means. However, it is clear that a reduction of all 24-hour concentrations currently in the 50-100 µg/m³ band to below 50 µg/m³ would reduce dramatically the number of exceedences of the EPAQS recommended limit.

For the winter data, it is possible to estimate approximately the extent of control of the major source of PM_{10} during episodes of high concentration, (ie vehicle emissions), in order to reduce a concentration of 100µg/m³ to 50 µg/m³. The Birmingham (Hodge Hill) data indicate that during episodes of high PM_{10}, the coarse particle fraction shows little dependence upon the episode concentration and is steady at about 15-20 µg/m³. The concentration of secondary PM_{10} is approximately 10 µg/m³, and thus allowing for the small fraction of the coarse particles associated with vehicle emissions and secondary PM_{10}, there is a background of about 25 µg/m³ which is not directly associated with vehicle emissions and will not respond to control of this source. Thus, to reduce a winter concentration of 100 µg/m³ to below 50 µg/m³ will require a reduction in the vehicle-emitted component of 75 µg/m³ to 25 µg/m³, ie a control of emissions of 67%. Control of

Figure 8.11 **Plot of Hourly $PM_{2.5}$ versus PM_{10} for Birmingham, Hodge Hill; April to July 1995.**

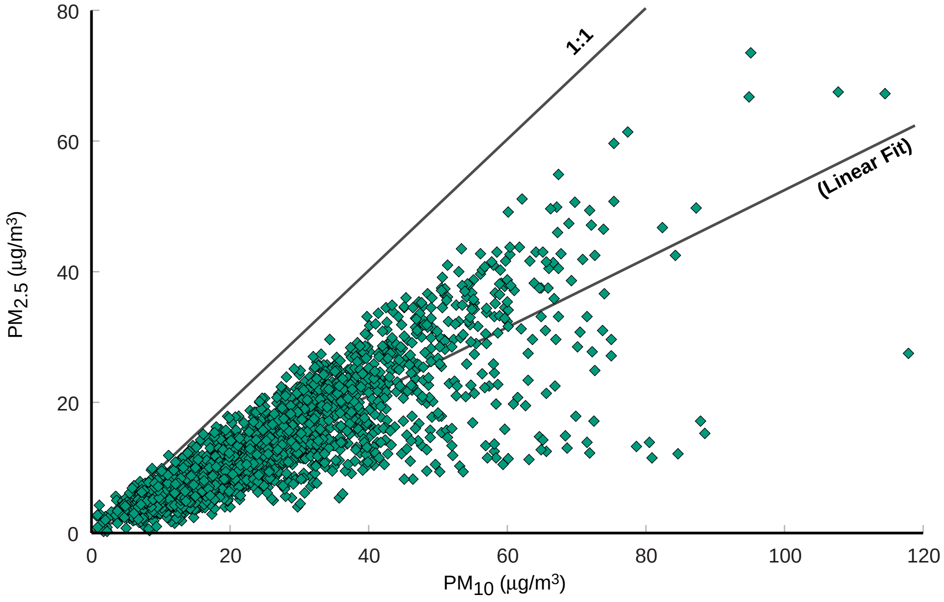
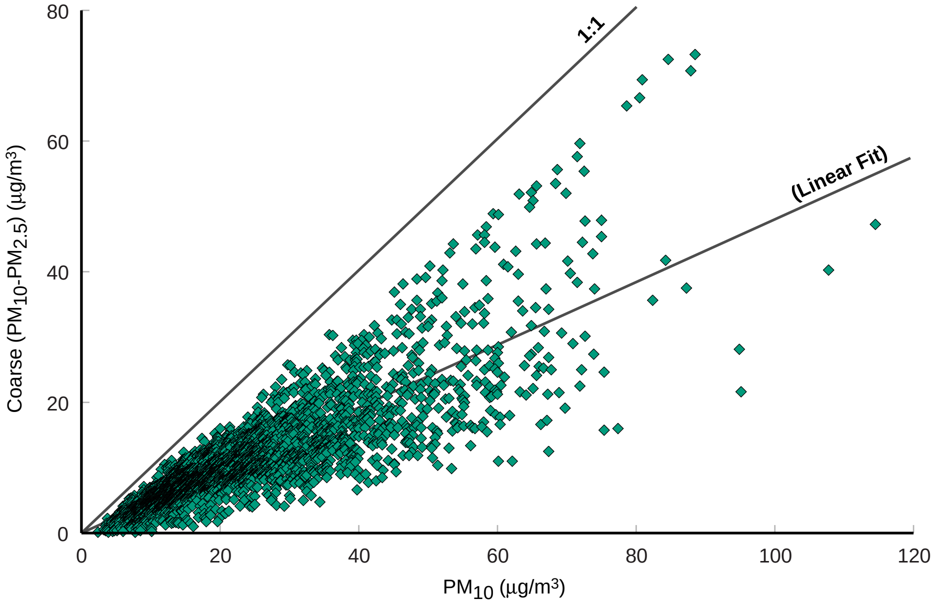


Figure 8.12 **Plot of Hourly Coarse Particles versus PM_{10} for Birmingham, Hodge Hill; April to July 1995.**



the precursors of secondary PM_{10} is estimated to deliver a reduction in the secondary component of about 4 µg/m³ by the year 2010. Taking this into account, the extent of control required for vehicle exhaust emissions is from 75 µg/m³ to 29 µg/m³, ie 61%. This analysis is applicable to the majority of UK urban areas, although in some such as Belfast a strategy to control emissions from combustion of solid fuel will also be needed. It should be noted that the analysis is based upon current measurements of PM_{10} at central urban background locations. Concentrations at near-road sites are substantially higher, by a factor of two or more, and an even greater degree of control of vehicle emissions will be required if concentrations at these site are to be reduced to below 50 µg/m³ as a 24 hour average.

The severe pollution episode which occurred in London in December 1991 represents some of the worst air quality experienced in the UK in recent years. Unfortunately PM_{10} measurements commenced in London in January 1992 and PM_{10} concentrations during the episode can only be estimated from concentrations of other pollutants. Using data for CO from the roadside Cromwell Road site and the inventory ratio of emissions of CO to PM_{10} from road traffic in London leads to estimates of maximum hourly and 24-hour average concentrations of PM_{10} of 221 µg/m³ and 155 µg/m³ respectively. Concentrations of CO and NOx at the background sites, Bridge Place and West London were little different from Cromwell Road and using a ratio of emissions of PM_{10} to CO from all sources leads to estimated hourly and 24-hour concentrations respectively of PM_{10} of 216 µg/m³ and 132 µg/m³ at Bridge Place and 281 µg/m³ and 174 µg/m³ at West London. These 24-hour concentrations far exceed 100 µg/m³ and indicate that the 61% control of road traffic exhaust emissions calculated above would not have been sufficient to bring air quality into line with the EPAQS recommendation. Indeed, following the methodology above, reduction of 174 µg/m³ at West London to 50 µg/m³ would require a reduction of traffic emissions of PM_{10} by over 80%.

In the summer months, the impact of vehicle exhaust emissions on PM_{10} is lower than in Winter and control of this source will have less impact. Currently, we have insufficient information on the episodicity of secondary particle components to estimate the degree of control required to reduce summer concentrations to below 50 µg/m³. However, given the greater contribution of coarse particles to summer concentrations of PM_{10}, it seems likely that the 39% reduction in secondary particle concentrations predicted for the year 2010 by the HARM model will be insufficient to guarantee achievement of the air quality standard.

8.8 CONCLUSIONS

All of the various approaches to source apportionment lead to the view that two sources of PM_{10} predominate. The first is road traffic, which contributes both to coarse and fine particle mass through resuspension of road surface dusts and exhaust emissions, respectively. The second major contributor is secondary aerosol, formed from emissions of sulphur and nitrogen oxides. In the winter, episodes of elevated PM_{10} are associated almost exclusively with excursions in fine $PM_{2.5}$ particles due to vehicle exhaust. In summer, there is a much greater contribution of coarse particles and secondary aerosol plays a greater role. The clear implications for control of episodic high concentrations of PM_{10} is that tighter limits on particle emissions from road traffic, and on secondary aerosol precursors will be essential if both summer and winter episodes are to be avoided.

8.9 KEY POINTS

- *Receptor modelling of the composition of urban total suspended particulate matter indicates the following major source categories: road dust and soil; vehicle exhaust; secondary aerosol and oil combustion; coal combustion; incineration and the metals industry, and road salt/marine aerosol.*

- *Secondary aerosol comprising mainly ammonium sulphate and ammonium nitrate is ubiquitous over the United Kingdom with highest concentrations in the south-east, progressively reducing by a factor of over two to the north and west.*

- *Carbon monoxide and nitrogen oxides may be used as tracers of vehicle emissions, allowing estimation of traffic exhaust related PM_{10} from regression analyses. These indicate that in winter on average 40-50% of urban PM_{10} arises from this source.*

- *The percentage contribution of road traffic to urban PM_{10} is typically higher in winter episodes.*

- *In summer, photochemically-generated secondary particles appear to be dominant, with a lesser contribution from vehicle exhaust than in winter.*

- *In winter the $PM_{2.5}$ fraction is very strongly traffic-related with coarse particles providing a relatively low and constant background.*

- *In summer the coarse fraction is more important, although episodes of high $PM_{2.5}$ do occur.*

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9 Effects of Airborne Particulate Matter

9.1 HEALTH EFFECTS OF NON-BIOLOGICAL PARTICLES

A detailed review of the possible effects of particulate air pollution on health has recently been completed by the Department of Health's Committee on the Medical Effects of Air Pollutants (COMEAP, 1995). These findings are summarised here. Readers are referred to the COMEAP report for details of the evidence considered and the detailed justification for the conclusions presented.

9.1.1 *Summary of COMEAP Report*

The evidence considered in the COMEAP report is concerned with effects on health of "suspended particulate matter" (SPM), comprising solid (soluble or insoluble) or liquid material present in the air in particles small enough to remain in suspension for some hours or days and liable to travel considerable distances from the source. This corresponds approximately with the size range of particles, typically less than 10 µm diameter, capable of entering the respiratory tract and reaching the deeper parts of the lungs.

SPM is not a defined entity: both chemical and physical characteristics vary widely with respect to source, location and time. There is no clear evidence as to whether effects on health are related to certain components or whether they represent non-specific effects of inhaled particles. Other pollutants or other factors in the environment, for example, changes in temperature, can affect the same health endpoints. It has proved difficult to do representative studies of the effects of the ambient aerosol under controlled conditions owing to the impossibility of recreating the precise particle mixture found in outdoor air. Studies of the effects of well defined small particles could be done and these would contribute useful baseline data; unfortunately few such studies have been reported. Because of this, there is little evidence other than from epidemiological studies. Some insight into possible mechanisms of effect have come from animal studies though no completely satisfactory explanation for the findings of epidemiological studies has yet been produced.

PM_{10} represents the size range of particles likely to pass the nose and mouth, $PM_{2.5}$ represents more closely the size range of particles able to reach the deeper parts of the respiratory tract. A significant proportion of the mass of material collected as PM_{10} is less than 2.5 µm in diameter. Particles of about 0.5 µm diameter are least likely to be deposited in the respiratory tract. Exercise may have a variable effect on particle deposition depending on particle size and pattern of respiration. The estimated typical adult deposition of particles in the PM_{10} range is about 250 µg/day: in terms of traditional toxicology of inhaled particles a small dose.

Some experimental studies, mainly in animals and at high concentrations, show that mixtures of particles with pollutant gases such as SO_2, NO_2 or O_3 have effects greater than those of the components separately, though it is not clear whether these results would apply at the low concentrations normally present in the environment. The adsorption of such gases, or of metals or acid-sulphates, on the surface of particles may be important. Animal studies also indicate a potentially important role for ultrafine particles (< 0.05 µm diameter). They are cleared only very slowly from the lung and they can penetrate the pulmonary interstitium inducing inflammatory responses. It has been suggested that allergenic material may be carried into the lung in association with particles though evidence is lacking.

Extensive studies of the effects of well characterised particles (eg, acid sulphates and sulphuric acid) have been carried out in volunteers. It has been demonstrated that at the concentrations likely to be experienced in the UK no effects would be expected in normal individuals. Exposure to concentrations of acid particles and gaseous pollutants has been shown to lead to an enhanced effect though the findings are not consistent. Subjects with asthma show enhanced non-specific reactivity following sulphuric acid challenge, but not, apparently, following sulphate challenge. However, all these changes in either lung volumes or bronchial responsiveness are, in general, small. The reasons for this may be in part methodological, but the evidence suggests that there is unlikely to be a large effect of acid or sulphate challenge on human subjects.

On the basis of findings from studies of pollution episodes in the 1950s to 1960s, when concentrations of suspended particulate matter, together with SO_2, were very high, it was not anticipated that adverse effects on health would be demonstrable at the much reduced concentrations of more recent years. However, a series of intensive studies, mainly in the United States, has demonstrated small changes in a wide range of health indicators, showing clearer associations with concentrations of particles than with other pollutants.

To some extent, the new findings have been dependent on the introduction of advanced statistical computing techniques, handling large data sets covering many variables. Such methods have passed into general use during the past 10-15 years. These procedures have been examined carefully and they are considered to be appropriate and the results are robust to a variety of statistical methods. It is unlikely that the findings of recent epidemiological studies are an artefact of the statistical methods employed.

Indicators of ill-health examined in relation to acute effects have included day-to-day variations in mortality, hospital admissions, emergency room visits, time off school or work, respiratory symptoms, exacerbations of asthma and changes in lung function. Of these various indices, the measurement of mortality is the most certain. In addition, effects on mortality have been particularly well studied and the results have been generally more consistent than those regarding the other indices. In most, associations with SPM, expressed at least in the more recent studies as PM_{10}, have been observed, within a relatively low range of concentrations of similar magnitude to those found in the UK today. It does not necessarily follow that the same types or sizes or components of particles are involved in these diverse effects. The composition of particles monitored as PM_{10} can vary widely from area to area and with time. However, the size of the estimated effects, particularly as regards effects on mortality, does not vary greatly with location.

Short-term variations in these health indicators have been demonstrated to be influenced by factors such as temperature and (even minor) epidemics of infections such as influenza, as well as possible effects of other pollutants, including SO_2 and ozone. Considerable efforts to control statistically for the effects of confounding factors have been made in recent epidemiological studies. For example, in the most recent studies in the United States, possible effects of air pollution have only been examined once all other identifiable variations in the health indicators have been accounted for. The likely success of the methods used inevitably depends on how well the confounding factors have been characterised and on this point there remains room for debate. Overall, control for confounding factors, in the more recent studies, is accepted as good. The possibility of some unmeasured confounding factor playing a role cannot be dismissed, but this is not considered likely.

Though the results of most epidemiological studies are described as providing exposure-response relationships, it should be remembered that, in general, they provide information on ambient concentration-response relationships across the population studied. In any population the range of personal exposure and consequently dose is likely to be considerable and monitoring the ambient concentration of a pollutant will provide only an estimate of exposure.

There is no clear indication that effects on health are restricted to specific types of particles. Findings from epidemiological studies have demonstrated associations with particles in a wide range of circumstances, including those in which primary emissions from motor vehicles, industrial sources or coal fires or where secondary aerosols derived from gaseous emissions (SO_2 and NO_x from power stations and other stationary sources with further NO_x from traffic) are important. It is unlikely, however, that coarse, wind-blown particles have a significant effect upon health.

It is well established from the reported studies that those with pre-existing respiratory and/or cardiac disorders are at most risk of acute effects from exposure to particles. It has been suggested that acute effects occur when air pollution worsens an acute condition such as a respiratory infection or heart attack in people with pre-existing chronic disease. There is no convincing evidence that healthy individuals are likely to be significantly affected by levels of particles found in ambient air in the UK.

In most of the statistical analyses of epidemiological studies, relationships have been expressed as regression equations from which the magnitude of effects linked with changes in pollution can be judged. An example, from a study in Detroit, indicates that a 30 µg/m^3 increase in PM_{10}, as a 24 hour average, was associated with a 3.5% increase in hospital admissions for pneumonia. This, of course, does not imply that exposure to such pollution initiated the illness: it should be considered as causal only through predisposing to, or worsening, the illness and precipitating the need for admission to hospital.

No evidence for thresholds of effect has appeared from the studies so far reported, though it should be noted that several studies are not powerful enough to examine the issue critically at low concentrations.

The principal question to consider in reviewing the rapidly expanding literature on effects of SPM is whether the statistical associations demonstrated indicate a causal role. There is certainly a remarkable degree of consistency and coherence in the direction and magnitude of findings from a diversity of studies, carried out in different localities in the United States and elsewhere, with a range of different health indicators and varying sources of pollution. COMEAP considers the reported associations between levels of particles and effects on health principally reflect an actual relationship and not some artefact of technique or the effect of some confounding factor. The indications that the association is likely to be causal are certainly strong.

The only major difficulty in reaching any firmer conclusion about causality is the lack of established mechanisms of action. The mass of SPM associated with adverse effects is very small, and while there is evidence relating to acute effects of some components, the fact that in epidemiological studies similar effects have been reported in localities with different types of suspended particulate matter suggests that there may be a non-specific effect of particles. The effects have not been explained in terms of the results of conventional inhalation toxicology studies but carriage of material on particle surfaces could play a role. It has been suggested, but by no means proven, that ultrafine particles (< 0.05 µm) may play a role. Such particles would be more prominent close to sources, before they had time to coalesce into the more stable accumulation mode, and they would represent only a small proportion of the mass of material measured as PM_{10}, though they would represent a high proportion of the number of particles present. Although reported studies indicate a range of effects, from small changes in ventilatory function or exacerbations of asthma through to increases in deaths among the elderly or chronic sick, it does not necessarily follow that the same components would be involved in each effect.

9.1.1.1 Implications for Public Health in the UK

COMEAP concluded that, in terms of protecting public health, it would be imprudent not to regard the associations as causal and also that the findings of the epidemiological studies of the acute effects of particles, which have been conducted in the US and elsewhere, can be transferred to the UK at least in a qualitative sense. However, it was considered that there are insufficient UK data available to allow direct extrapolation and reliable estimation of effects in the UK.

It would be possible, but unwise, to take a weighted average of the results of the published studies and apply this to conditions in the UK. The coefficient produced by Schwartz (1994) with regard to effects of particles on mortality was 1.06 (CI: 1.05-1.07) for a 100 µg/m^3 change in TSP. No similar figure based on structured meta-analysis and providing confidence intervals is available with respect to PM_{10}. Because of this, COMEAP felt it would be unwise to offer a single coefficient with regard to effects on mortality or other indices of ill health. The reader is referred to the COMEAP report where a collection of estimates derived from a wide range of studies is presented. It should be recalled that estimates based on studies reported in this collection are likely to provide only a first approximation to the actual effect in the UK. COMEAP recommend that studies should be undertaken urgently to allow better quantitative predictions to be made. In comparison with other uncontrolled factors, eg, variations in temperature, the effects of day-to-day variations in levels of particles are small.

9.1.1.2 *Chronic Effects*

With regard to indicators of possible chronic effects on health as a result of exposure to particles, in the UK, there has been a long-established association between the prevalence of, and mortality from, chronic respiratory disease (bronchitis) and exposure to the SO_2/particle complex associated with coal-burning. The role of the particulate component has remained uncertain and other factors, notably smoking, have been shown to be of major importance. Disentangling the roles of multiple factors operating throughout life has proved to be a difficult task, but in some recent US studies, it has been possible to follow selected population groups for a number of years, relating death-rates among them to local pollution levels. Associations have been found to be closer with concentrations of particles than with those of other pollutants, but in view of uncertainties about the possible relevance of (higher) exposures to pollution earlier in life and the difficulties in fully adjusting for confounding factors, quantitative assessments are in doubt. The lower prominence given to this aspect of the effects of particles on health in the COMEAP report reflects the lack of data rather than the potential importance of possible effects on the public health.

Evidence regarding the effects of long term exposure to particles on health is less well developed than that regarding the acute effects. The possibility of confounding in such studies is considerable and it is difficult to estimate the exposures of individuals over relevant time periods. Here again the results of recent US studies are probably transferable to the UK in a qualitative sense though confidence in the accuracy of the predictions is lower than with regard to the acute effects of particles. Though the evidence is limited COMEAP advised that it would be prudent to consider these associations as causal.

There is little evidence to show that exposure to atmospheric particles contributes significantly to the burden of cancer in the UK. The presence of genotoxic carcinogens in particles means that such a contribution cannot be ruled out, though it is likely to be exceedingly small.

9.1.1.3 *Conclusions*

The COMEAP report ended with the following brief conclusions:

"The Committee considers the reported associations between levels of particles and effects on health principally reflect an actual relationship and not some artefact of technique or the effect of some confounding factor.

In terms of protecting public health it would be imprudent not to regard the demonstrated associations between levels of particles and effects on health as causal.

We find it difficult to reach a firmer conclusion about causality due to the lack of any established mechanism of action.

We believe that the findings of the epidemiological studies of the acute effects of particles, which have been conducted in the US and elsewhere, can be transferred to the UK, at least in a qualitative sense.

It as accepted that insufficient UK data are available to establish the reliability of quantitative predictions of the effects of particles upon health in the UK.

We consider that results of recent US studies of the effects of long-term exposure to particles are probably transferable to the UK, though confidence in the accuracy of the predictions is lower than with regard to the acute effects. Although the evidence is limited, we advise that it would be prudent to consider these associations as causal.

There is no convincing evidence that healthy individuals are likely to be significantly affected by levels of particles found in ambient air in the UK."

9.2 THE EFFECTS OF PARTICULATE MATTER ON VISIBILITY

Good visibility away from towns and cities in Europe is generally around 40-50 km (Horvath, 1995) and on very rare occasions may be as great as 100-150 km. The light seen by an observer consists of radiance transmitted directly from the target plus radiance along the path. The transmitted light decreases as light is either scattered or absorbed along the path and visibility is thus reduced. As the range of vision increases, path radiance (light scattered into the sight path) increases and the light transmitted from the target decreases, causing a decrease in the visibility. Transmittance is governed by the extinction coefficient of the atmosphere, which is made up of two terms, one for particles and one for gases and each of these is made up of two further terms, one accounting for scattering and one for absorption of light.

Absorption of visible light is most effective at particle diameters around 1 µm, as these particles have a diameter close to the wavelength of light. Scattering of light is effective over a range of particle diameters but is dominated by aerosol of between 0.2 and 2 µm. These aerosol particles may be particularly affected by changes in relative humidity, as deliquescence may occur as humidity increases, causing the formation of a haze which may decrease visibility. Studies have been conducted into visibility reduction by identifying individual substances within the atmosphere and applying an extinction coefficient to each of these. These studies suggest that scattering is the dominant process for light extinction, with absorption being responsible for between 10% (in rural areas) and 30% (in urban areas) of extinction.

Atmospheric visibility is defined as that distance at which a black object can be seen against the horizon. Particles suspended in the atmosphere between the observer and the object act to reduce the contrast and thus reduce the visual range. From studies in the south of England, Lee (1990) has suggested that the most important source of long-term changes in visibility is changes in primary emissions within the UK rather than the long distance transport of polluted air from continental Europe. However it was also found that wind directions and circulation types most favourable for the transport of pollution from central Europe are those in which there has been least improvement, showing that the continent is a significant source of air pollution during the summer.

Gomez and Smith (1987) found a decrease in fog frequency in Oxford after the implementation of the Clean Air Act, despite that the fact that there were no increases in winter sunshine levels over the same study period. Clarke and Papapanayotou (1987) made measurements of optical properties of roadside aerosol in the city of Leeds, and found that the absorption coefficient of aerosol at the roadside was three times that on a rooftop 30m above the road. The authors also suggested that smoke values could be used to predict the atmospheric absorption coefficient, and that in this way smoke data could be used to assess the importance of optical absorption on visibility degradation.

Lee (1994) has also analysed visibility trend data from 22 sites in urban, coastal and inland rural locations. He found that visibility at nearly all sites had increased over the period 1962-1990, with the largest improvements being in urban areas where median visibility often now approached or exceeded values at rural locations. Visibility increases at rural sites were most marked in the north of the country away from both major UK and continental sources. The improvement in visibility in southern England is less marked and it is speculated that this may be due to increased frequency of photochemical episodes, and the long range transport of pollutants from the continent. Harrison and Colbeck (1984) also found that high concentrations of secondary pollutants caused a decrease in visibility in north-west England, the best correlation being with the ammonium concentration.

Research currently underway at The University of Birmingham is investigating the influence of PM_{10} concentrations on visibility, and is looking at long term trends in visibility. Figure 9.1 shows the increase over time in visibility as represented by percentiles of visual range for the Elmdon reporting station at Birmingham airport. The graphs show that for 10th 50th and 90th percentiles the visibility has

Figure 9.1a Visibility Trends, Elmdon Summer.

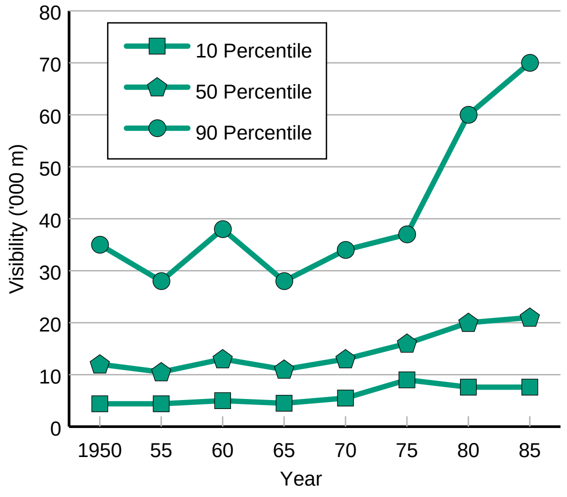
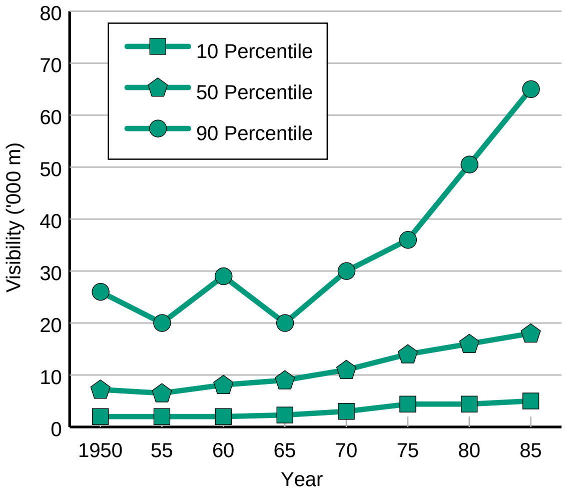
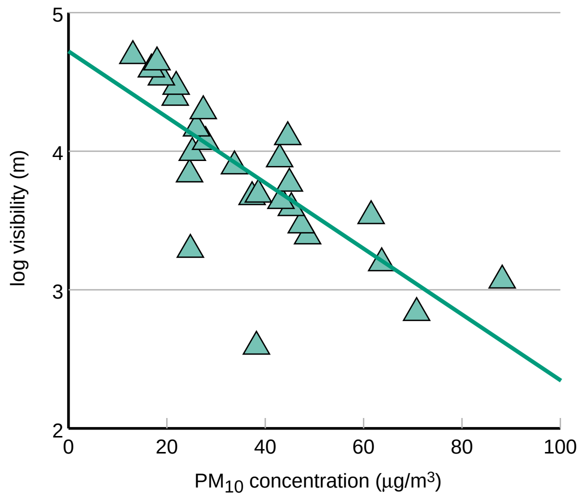


Figure 9.1b Visibility Trends, Elmdon Winter.



increased appreciably since 1950 during both Summer and Winter periods.

Figure 9.2 PM_{10} Concentration vs log Visibility, 15.00 hours Readings for Birmingham.



Note: Visibility data are for Edgbaston, and PM_{10} data for Centenary Square in the city centre.

PM_{10} data collected at the Birmingham city centre AUN site have also been related to visibility data provided by the University Weather Service, from a site approximately 3 miles south of the city centre. There are problems associated with the analysis of visibility data however, due to the fact that the data are recorded by comparing visibility against markers (such as buildings or landmarks) at known distances from the observer, hence the data appear as a frequency distribution. The data for Birmingham for 1993 at 15.00 show a high degree of correlation between PM_{10} concentration and visibility ($r^2 = 0.57$) when a mean PM_{10} concentration is taken for each visibility class (Figure 9.2), indicating that particulate matter exerts a strong control on visibility. Similar relationships can be found at different times of day, although other meteorological parameters such as relative humidity will influence visibility to a greater extent.

9.3 NUISANCE FROM SOILING

The issues of nuisance from smoke, fumes and odour were considered by QUARG in their First Report (Section 2.9) and Second Report (Section 4.9). The specific issue of the effects on buildings and materials were addressed in Sections 2.10 and 4.11 respectively.

Soiling is generally regarded as the dirtying or blackening of surfaces by particulates. Road vehicles contribute to urban soiling mainly through the deposition of exhaust particulates onto surfaces. Vehicles are a major source of particulate matter and black smoke in urban areas (QUARG, 1993) with diesel emissions widely regarded as having a greater blackening propensity than petrol engine emission and coal fires. Assessment of the relative contributions of various sources to urban soiling is complex and may depend on a number of factors, such as:

- the particular soiling/dirt problem under investigation;
- the blackness per unit mass of smoke;
- the particle size distribution;
- the chemical nature of the particles;
- substrate-particle interfacial binding;
- surface orientation;
- micrometeorological conditions.

Recent research (Williams and McCrae, 1995) has indicated that the soiling of buildings is a low priority environmental issue compared to other concerns the public have about their local environment, as displayed in Table 9.1. The relative rankings are based on the number of respondents from each location who were very/extremely worried about each issue. The rankings are averages and run from 1 to 10, with 1 representing the highest level of concern and 10 the lowest. The low ranking of building soiling is unexpected given its very visible impact, especially on high profile historic buildings such as St Paul's Cathedral, and the economic costs of cleaning soiled buildings. However, although this issue is relatively lowly ranked in comparison to other local environmental issues, it still generates a significant amount of public concern in certain areas of the country. The research showed that on average, 48% of respondents in UK cities claimed moderate to extreme disturbance from building soiling, with the range extending from 12-70% depending upon area and respondent group. In general, 20-40% of respondents blamed the soiling of buildings upon road traffic pollution. These figures are in good agreement with those of Ball and Caswell (1983), who suggested that one-third of the UK population were bothered by vehicle-induced soiling of property in the early 80's.

This evidence, together with other data showing that the physical presence of road traffic is as important as the presence of pollutants, may indicate that health and safety concerns are more important to the public than aesthetic issues associated with diesel pollution.

The Middlesex University team have conducted a series of exposure studies (Hamilton and Mansfield, 1992) using stone tablets and painted wood, in a road tunnel and in the ambient environment (sheltered and unsheltered). The existing models predict an exponential decrease of reflectance with time and these were satisfactory for predicting soiling in a tunnel but not in an ambient situation. Satisfactory empirical relationships for ambient exposures involve a loss in reflectance ΔR which varies with the square root of the exposure time.

Table 9.1 Rank Order of Respondent Concern About Local Environmental Issues at Selected UK Sites.

Issue	**Birmingham**	**Cardiff**	**Coventry**	**Edinburgh**	**Sheffield**	**Wood Green**	**Overall**
Litter & Rubbish	2.8	2.2	2.0	4.0	1.2	1.3	2.3
Amount of Road Traffic	1.8	1.8	4.0	1.2	2.2	4.0	2.4
Smoke, Fumes & Odour	2.0	3.0	1.8	2.2	3.5	2.7	2.5
Dog Mess	3.8	2.8	2.0	3.0	4.8	2.0	3.1
Dust & Dirt	5.8	5.2	6.8	5.0	5.0	4.3	5.4
Ugly/Disused Buildings	6.5	6.2	5.2	8.0	6.0	7.3	6.5
Noise	5.8	7.8	6.8	6.0	8.0	7.7	7.0
Graffiti	7.8	8.2	8.2	7.5	5.0	6.7	7.3
Smog	8.5	8.0	7.5	8.0	7.8	8.3	8.2
Blackening of Building Walls	9.5	9.5	9.2	9.0	9.8	9.7	9.4

Rainfall generally produced a cleaning effect but the relationship is complex and cannot be quantified at present.

9.4 EFFECTS OF ATMOSPHERIC AEROSOLS ON CLIMATE CHANGE

Atmospheric aerosol in the troposphere influences climate in two ways: directly, through the reflection and absorption of solar radiation, and indirectly through the modification of the optical properties and lifetime of clouds. Estimation of the radiative forcing induced by atmospheric aerosols is much more complex and uncertain compared with the well-mixed greenhouse gases because of the complex physical and chemical processes involved with aerosols and because of their short lifetimes which make their distributions inherently more inhomogeneous.

The haze visible from high-flying aircraft over continental areas is a dramatic manifestation of the important role played by the atmospheric aerosol in scattering sunlight. Much of this aerosol is derived from human activities and the increase in optical depth over and downwind of industrial regions is significant compared with the natural background. The major contributions to the man-made component of the aerosol optical depth arise from sulphates produced by the oxidation of sulphur dioxide released by fossil fuel combustion and from the oxidation of the organic substances produced by biomass burning.

The net global mean radiative forcing due to the increase in atmospheric aerosols due to human activities, including fossil fuel combustion and biomass burning, since pre-industrial times is negative, exerting a cooling influence on the climate system. The Intergovernmental Panel on Climate Change estimates this influence to be -0.5 W/m^2 globally, or about 20% of the total effect of greenhouse gases. However the effects of aerosols are highly regional, reaching a maximum over industrialised land masses. The IPCC have only given firm estimates for the direct, scattering effect. The indirect effect is highly uncertain and is in the range 0 - 1.5W/m^2.

Human activities lead to the emission of black soot or carbon particles whose main effect is to absorb radiation rather than to scatter it. Such aerosols can exert a warming effect on the climate system although it is very much smaller in magnitude than that due to the greenhouse gases. The IPCC estimates the radiative effect of soot aerosols to be around +0.1 W/m^2, or approximately 5% of total greenhouse gas forcing. This is accounted for in the total forcing influence of -0.5 W/m^2 above.

The impact of aerosol on the optical properties of low level clouds has been demonstrated in localised observations but the global scale impact has yet to rigorously quantified. These indirect effects of aerosols on climate depend on complex processes involving aerosol particles and the nucleation and growth of cloud droplets. These effects are expected to be smaller for additional aerosol introduced into already polluted air. There is some observational evidence to suggest that the mean sizes of cloud droplets are larger in the Southern Hemisphere where tropospheric aerosol concentrations are generally lower than in the Northern Hemisphere where aerosol concentrations are generally higher.

Estimates of the indirect effect of sulphate aerosols are somewhat larger than the direct effect, though significantly more uncertain. Taken together, both direct and indirect, both scattering and absorption, have led to a negative radiative forcing since preindustrial times which is about one half to three-quarters that due to the long-lived greenhouse gases. It is likely that much of this radiative forcing is concentrated over continental areas and that it has a significantly different spatial pattern to that of the greenhouse gases.

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10 Conclusions

The study of airborne particulate matter has lagged behind research on most of the other common air pollutants. This has probably happened because particulate matter was not perceived as a significant threat to health once the extreme pollution characterised by the London smogs was abolished. The other problems associated with airborne particulate matter, such as soiling and visibility degradation were not perceived as major issues in comparison to health concerns relating to pollutants such as sulphur dioxide, nitrogen dioxide and ozone. However, the recent epidemiological work pioneered by the Harvard School of Public Health, but now being repeated around the world, has built a strong case for believing that fine airborne particles have a serious detrimental influence on health. This has led to a burgeoning of interest in particulate pollutants, although the base of data has been severely limited.

For reasons which were sound at the time, airborne particulate matter in the UK atmosphere has traditionally been measured by the Black Smoke method. This nowadays gives no useful indication of the mass of particles per unit volume of air, and it was a far-sighted decision by the Department of Environment to introduce automatic gravimetric TEOM monitors for particulate matter when the Enhanced Urban Network (now part of the Automatic Urban Network) was established, starting in 1991. This Network, which is still growing, has provided invaluable high quality data upon the concentrations of PM_{10} particles in our major towns and cities. The data available to the policy makers and research workers from this network, to be made available in due course to the general public, probably equals that of any other country in the world and far exceeds the quality of data available in many other developed countries in terms of the time response and speed of availability to the user.

Airborne particles in the UK atmosphere arise from a wide variety of sources. Receptor modelling methods, which depend upon hour-to-hour and day-to-day variations in the concentrations and chemical composition of the airborne particles, give a useful indication of the diverse range of sources. These show road transport to be a very major source of particles in urban air, both through exhaust emissions and coarse dust resuspended from the road surface by atmospheric turbulence induced by the passage of traffic. Traffic also generates particles from the wear of rubber tyres and of the road surface itself. Both sea spray and de-icing salt lead to the presence of sodium chloride particles in the atmosphere, even at locations remote from the sea. The other main source of particles arises from the emission of sulphur dioxide, mostly from power stations and other industry, and of nitrogen oxides from road traffic, power stations and other combustion sources. These gases are oxidised in the atmosphere to form sulphuric and nitric acids which are neutralised with atmospheric ammonia to form the so-called secondary aerosol of mainly ammonium sulphate and ammonium nitrate. Because of its rather slow formation and long atmospheric lifetime, concentrations of secondary particles are far more uniform across the UK than the primary emissions from road traffic, which are concentrated mainly in urban areas. The European continent contributes significantly to the airborne loading of secondary particles in the UK atmosphere. Concentrations of secondary aerosol are highest in the South-East of the country, diminishing towards the North and West. Road transport contributes to secondary aerosol concentrations through emissions of NO_x. In London, a very high proportion of PM_{10} is accounted for by the sum of vehicle exhaust emissions and secondary particles.

Airborne particles vary greatly in their size and this influences their atmospheric behaviour. Particles emitted from combustion sources and formed from gas to particle conversion are initially very small in size (around 0.02 µm diameter) and very numerous. These particles have the greatest influence on the atmospheric particle number count, which in polluted locations often exceeds 100,000 particles per cubic centimetre. These very fine nucleation mode particles rapidly coagulate with other particles in the air to form the accumulation mode, comprising particles of intermediate size which are capable of existing in the atmosphere for 10 days or so, which can therefore be transported over very large distances by the wind. Most particles arising from human activity fall into these two size categories which have the greatest implications for human health. Airborne dusts produced by mechanical disintegration processes such as grinding and milling, break-up of soil surfaces by the wind and formation of sea spray from breaking waves tend to be appreciably larger in size and form the coarse particle fraction within PM_{10}. Whilst such particles arise in part from human activity, such as dusts resuspended from the road surface by passing traffic, a major proportion is probably natural in origin and hence very difficult to subject to controls. Indeed, it is only because the UK has a relatively wet climate and much of the ground is covered in vegetation that airborne concentrations of wind-blown dust are not much higher.

Emissions inventories are well able to quantify sources such as road traffic exhaust and power station emissions. They also include such activities as quarrying and the generation of particles from tyre wear; the associated emission factors must be far less certain, however. The inventories attribute an appreciable proportion of airborne particulate matter nationally to road traffic emissions and show that in urban areas the influence of road traffic is very much greater. Emissions from diesels make up far the major part of the total particle mass from road traffic; the modern catalyst-equipped petrol engine is currently the cleaner option with respect to PM_{10} emissions. The inventories are not well able to accommodate secondary particles formed in the atmosphere, but high quality numerical models of atmospheric chemistry and transport are available, which not only give a good capability for predicting current concentrations of secondary components in the atmosphere, but can also predict the impact of future controls on SO_2 and NO_x emissions upon airborne concentrations of secondary PM_{10}.

Control strategies for airborne particulate matter must address the sources of particles contributing to episodes of elevated concentrations. In some areas, these include coal burning, and locally may include construction and demolition activities as well as industrial operations like iron and steel production and minerals extractions. In the great majority of urban areas, however, vehicle emissions, predominantly of fine particles ($PM_{2.5}$) are the dominant source. Simultaneous measurements of PM_{10} and $PM_{2.5}$ show that in winter road traffic contributes little to coarse particle concentrations in the atmosphere, and also that coarse particles rarely contribute significantly to raised concentrations of PM_{10} in the urban atmosphere. Coarse particles are also of limited atmospheric lifetime, and hence travel distance, and may thus give rise to local problems, but have little impact on a city-wide or national basis. The sources are largely natural and/or diffuse, and control strategies need careful consideration in the light of this.

There are a number of reasons why control strategies for PM_{10} in urban areas should concentrate on the fine $PM_{2.5}$ fraction which include:

- The most severe excursions in PM_{10} occur in the winter months when $PM_{2.5}$ is the predominant fraction.

- As noted above, it is excursions in $PM_{2.5}$ which lead to the majority of elevated concentrations of PM_{10}, especially in the winter months.

- The sources of $PM_{2.5}$ are well defined and are controllable.

The work in which $PM_{2.5}$ and PM_{10} have been measured simultaneously over a period of many months clearly indicates that road traffic exhaust emissions and secondary aerosol together can account for essentially all of the atmospheric loading of $PM_{2.5}$. It follows that these are the sources which should be the main target if controls on PM_{10} are required.

Using data upon winter concentrations of PM_{10} it is possible to calculate the extent of control required to reduce 24-hour PM_{10} concentrations of 100 $\mu g/m^3$ to meet the EPAQS recommended standard of 50 $\mu g/m^3$. The reasoning has been set out in Chapter 8 and leads to an estimated requirement of about 60% control of vehicle-emitted particulate matter if the majority of central urban background sites are not to exceed 50 $\mu g/m^3$, or are to exceed it only very infrequently. The projected reduction in emissions of particulate matter from road traffic by the year 2010 are about 50% but this gives no ground for complacency. Firstly, the projected reductions in particulate matter emissions assume that renewal of the vehicle fleet will continue at a rate comparable to that in the past, and that new vehicles will conform to the EC emissions limits and continue to do so even as they age. Secondly, the dataset from which current airborne concentrations are taken comes from measurements at central urban background locations. To meet the EPAQS standard at roadside sites, where concentrations are typically double the urban background, and during extreme episodes will require a far greater degree of control. For example, to have limited 24-hour average PM_{10} to below 50 µg/m^3 in the December 1991 pollution episode in London is estimated to require a reduction of over 80% in road traffic exhaust emissions.

Data based on fixed 24-hour measurements of PM_{10} listed in Table 6.17 indicate that measures which effect a reduction of all 24-hour PM_{10} concentrations currently in the 50-100 µg/m^3 band to below 50 µg/m^3 would have a dramatic influence upon air quality. Exceedences of 50 µg/m^3 over fixed 24-hour periods would drop from 442 to just 5 in the 1992-1994 data from the network listed in Table 6.17 if Belfast, which is exceptional due to the continued combustion of solid fuels in domestic premises, is omitted. This requires a 50% cut in peak concentrations of PM_{10}, although to bring all rolling 24-hour concentrations below the 50 µg/m^3 recommended by EPAQS would require a larger reduction. Whilst the majority of exceedences of 100 µg/m^3 (24 hour average) occur in winter, concentrations in the 50-100 µg/m^3 band occur in all months of the year. In summer, the seasonal average contribution of vehicle emissions to PM_{10} is considerably less than that in winter, and the significant correlation of peak hourly PM_{10} with peak hourly ozone clearly indicates the importance of photochemically produced secondary particles at this time of year. Coarse particles can also make a substantial contribution in summer. Numerical projections using the HARM model indicate that a 39% reduction in secondary particles is likely to be achieved by the year 2010 on the basis of agreements already in place for the control of sulphur and nitrogen oxides. The background PM_{10} due to coarse particles is typically greater in summer than in winter, and although our understanding of the episodicity of PM_{10} pollution due to secondary particles is not as complete as for vehicle-emitted particles in winter, it seems certain that a level of control of secondary particles well in excess of 39% will be needed to reduce summer PM_{10} to below 50 µg/m^3 given the high background of coarse particles. A complementary strategy would involve control of coarse particles also, but current understanding of the sources and hence implications for control is insufficient in relation to coarse particles.

Detailed analyses of the air quality data clearly show the immense importance of road traffic emissions in influencing $PM_{2.5}$ and PM_{10} concentrations when these are elevated. In winter, a dramatic reduction of hourly exceedences of 50 µg/m^3 of PM_{10} could be achieved solely by limiting road traffic exhaust emissions. Currently, diesel vehicles, in particular trucks and buses, are the main contributor to PM_{10} emissions from this sector. In our Second Report, the results of predictive calculations of future emissions of particulate matter from road transport were presented. These indicated the importance of control of diesel vehicles in reducing emissions of particulate matter from road traffic. The revised projections of future emissions included in this report show that measures currently in place will not deliver a sufficient reduction in primary emissions to ensure that all concentrations fall within the EPAQS recommended limit, even by the year 2010. These projections are based upon a modest level of market penetration by diesel cars, and any increase in market share for diesels would inevitably make matters worse as the current technology diesel car emits far more particulate matter than the modern petrol car, and although technological development of the diesel will narrow the gap, there is no current prospect of the diesel improving beyond the petrol car. Additionally, the diesel car emits more nitrogen oxides than the near-equivalent petrol vehicle with a three-way catalyst and hence the impact of more diesel cars in the parc upon future secondary particle concentrations will also be deleterious.

In its eighteenth report on transport and the environment, the Royal Commission on Environmental Pollution recommended the implementation of the most stringent controls practicable on particulate matter in the Stage III emission limits to be introduced by the European Commission in the year 2000. The Royal

Commission also drew attention to the problems of simultaneous control of both particulate matter and nitrogen oxides from the diesel and recommended that limits on one pollutant should not be at the expense of the other. It is clear from the data and analyses presented in this report that stringent additional controls both on particulate matter from road transport, and upon the emissions across Europe of sulphur and nitrogen oxides responsible for the formation of secondary particles in the atmosphere, will be essential if UK urban particulate matter concentrations are to be reduced in line with the recommendation of the Expert Panel on Air Quality Standards. Additionally, in some localities, further controls on burning of coal and other solid fuels, and of emissions from major point sources will also be required.

Research Recommendations

Inventories

1. Further studies of emission factors for particulate matter from road vehicles, especially heavy duty vehicles are needed. This should include tyre and brake wear as well as exhaust emissions. Where possible, on-the-road measurements are preferable.

2. Size differentiated emission factors for other sources of primary particulate matter such as construction work, quarrying, agriculture and resuspension from road surfaces should be determined under typical UK conditions.

3. Inventories of primary PM_{10} are needed for a greater number of urban areas.

Monitoring and Chemistry

4. A number of PM_{10} monitoring stations should be located in rural areas to establish rural concentrations and to evaluate particulate matter concentrations in air arriving from the European continent.

5. Monitoring of $PM_{2.5}$ should be carried out at a number of Automatic Urban Network stations.

6. Measurements of particle number count should be carried out on an experimental basis at sites including urban, rural and roadside locations.

7. Measurements of size distribution of particles in the UK atmosphere in terms of particle number and mass, and for individual chemical constituents, should be made.

8. Studies of personal exposure to airborne particles should be conducted, including co-exposure to particles and airborne allergens.

9. Co-located measurements of TSP, PM_{10}, $PM_{2.5}$ and black smoke should be conducted at selected sites to establish inter-relationships in relation to particle chemical composition.

10. Studies of the surface chemical composition of particles are relevant to a full comprehension of their health impact, and are hence recommended.

11. Studies of the spatial distribution of PM_{10} and $PM_{2.5}$ across urban areas are needed.

Receptor Modelling and Source Apportionment

12. Detailed studies of the full chemical composition of representative samples of PM_{10} are required.

13. Daily samples of PM_{10} and $PM_{2.5}$ should be analysed for selected chemical species indicative of specific sources over at least a year at representative sites.

14. Studies should be undertaken of the composition and sources of coarse particles, whose origins are currently poorly defined.

15. Studies of the influence of meteorological factors upon concentrations of PM_{10} and its specific components are recommended.

Effects of Particulate Matter

16. The role of urban particles in influencing cloud and fog formation and visibility deserve attention.

17. Further detailed studies of the health effects and mechanism of action of PM_{10} in humans are required. Specific recommendations appear in the report of COMEAP.

Glossary of Terms and Abbreviations

Accumulation mode
A part of the size spectrum of airborne particles, between approximately 0.1-2 µm diameter, in which particles have a long atmospheric lifetime

Aeroallergens
Airborne antigens that cause allergy in a sensitive individual, e.g. pollen, house dust mite

Aerodynamic diameter
The aerodynamic diameter of a particle is the diameter which the particle would have if it were to be spherical in shape, to be of unit mass and to have the same sedimentation rate.

Aerosol
An atmosphere containing particles which remain airborne for a reasonable length of time

Black Smoke
Non-reflective (dark) particulate matter, associated with the smoke stain measurement method

Brownian motion
Constant small movement of suspended bodies due to bombardment by surrounding molecules

Coarse particle mode
A part of the size spectrum of airborne particles, greater than about 2 µm diameter, in which particles have arisen mostly from disintegration of bulk solid and liquid materials

Coarse Particles
Particles within the coarse particle mode. In this report, often refers to particles in the 2.5-10 µm size fraction.

Count Median Diameter (CMD)
Term used to characterise the size distribution of particles in an aerosol. 50% of particles are of diameter less than the count median diameter

Fine Particles
Particles smaller than about 2 µm diameter which arise mainly from condensation of hot vapours and chemically-driven gas to particle conversion processes. In this Report, often refers to the $PM_{2.5}$ fraction.

Geometric standard deviation
Term used to describe size distribution of particles conforming to a log-normal function

Hygroscopic growth
Growth of particles due to uptake of water from the atmosphere

Inhalable particles
Particles which may be breathed in. “Inhalability” is the orientation-averaged aspiration efficiency of the human head. (Also termed inspirable)

Mass concentration
The concentration of particles in air expressed as mass per unit volume

MMAD
Mass Median Aerodynamic Diameter. Term used to characterise the distribution of sizes of particles in an aerosol. MMAD is the size where half the mass of the cloud is contained in particles of aerodynamic diameter smaller than the stated aerodynamic diameter and half in larger particles

MMD
Mass Median Diameter. As for MMAD except that the diameter considered is the actual diameter rather than the aerodynamic diameter

Monodisperse
Term used to describe an aerosol containing particles of only one size

Nucleation mode
A part of the size spectrum of airborne particles, below about 100 nm diameter, in which particles arise mostly from fresh emissions from combustion processes, and gas to particle conversion

Number concentration
The concentration of particles in air expressed as number of particles per unit volume

Number median diameter (NMD)

Term used to characterise the distribution of sizes of particles in an aerosol. The NMD is that size where half the total number of particles are of diameter greater than NMD and half of diameter less than NMD (same as count median diameter)

Photochemical smog

Smog caused by the formation of particles due to a chemical reactions driven by sunlight

PM$_{2.5}$

Particulate matter less than 2.5 µm aerodynamic diameter (or, more strictly, particles which pass through a size selective inlet with a 50% efficiency cut-off at 2.5 µm aerodynamic diameter)

PM$_{10}$

Particulate matter less than 10 µm aerodynamic diameter (or, more strictly, particles which pass through a size selective inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter)

PM$_{15}$

As PM$_{10}$, but with 15 µm as the cut-off

ppb

Parts per billion, 1 part by volume in 10^9

ppm

Parts per million, 1 part by volume in 10^6

Relative humidity

Actual vapour pressure/saturated vapour pressure expressed as a percentage. A measure of the degree of saturation of the air with water vapour

Respirable Particles

Particles which can penetrate to the unciliated regions of the deep lung.

Smoke

Particulate matter, <15µm, derived from the incomplete combustion of fuels.

Suspended Particulate Matter (SPM)

A general term embracing all airborne particles.

TEOM

Tapered Element Oscillating Microbalance, an instrument for the continuous measurement of suspended particulate matter in air

Thoracic particle mass

Describes that fraction of the particles which penetrates beyond the nasopharynx and larynx

Total Suspended Particulate (TSP)

A term describing the gravimetrically determined mass loading of airborne particles, most commonly associated with use of the US high volume air sampler in which particles are collected on a filter for weighing

Troposphere

Layer of the atmosphere extending upwards from the earth's surface for about 10 km

TSP

Total suspended particulate

Ultrafine particles

Particles of less than 50 nm diameter (some workers use 100 nm)

Terms of Reference and Membership

TERMS OF REFERENCE

1. The UK Review Group on Urban Air Quality is a working group of experts established by the Department of the Environment to review current knowledge on urban air quality and to make recommendations to the Secretary of State for the Environment.

2. The initial objective of the Group is to prepare a review of urban air quality and how it is assessed in the United Kingdom especially in relation to public exposure, and how this information is passed on to the public. To this end the Group will consider:

   i) the pollutants measured,

   ii) the extent of monitoring networks,

   iii) the consistency of data,

   iv) the types and location of monitoring equipment and

   v) any other relevant material.

3. The longer term objectives of the Group will be to:

   i) perform a rolling review of the subject in the light of scientific and technological developments,

   ii) consider, in the light of national and international guidelines and advice, the need to add or subtract sites from the networks and the need for additional networks for different pollutants and

   iii) to consider arrangements for the public availability of data.

4. The Group will identify areas of uncertainty and recommend where further research is needed.

5. The Group will make recommendations for changes to relevant monitoring networks and public information systems.

6. The Group will act as an informal forum for the discussion of research plans and results.

7. The Group will act as a point of liaison with relevant international bodies.

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