THE UNIVERSITY
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CHARACTERISATION OF PARTICULATE MATTER IN THE UNITED KINGDOM

(REF. CPEA 6)

Literature Review

The University of Birmingham

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EXECUTIVE SUMMARY

This review has been conducted in order to set the context for further research on the chemical composition and source attribution of airborne particulate matter in the United Kingdom. Currently, the UK is subject to Limit Values for particulate matter set by the European Union with a view to the protection of public health.

The European Union specifies a manual reference method for particles measured as PM_{10} mass. Currently in the UK the Automatic Urban and Rural Network uses the automated TEOM instrument which measures PM_{10} concentrations typically some 15-30% lower than the reference method. No simple correction factors appears to be feasible and systems are currently under investigation designed to correct TEOM data for the semi-volatile losses which are primarily responsible for the divergence from the reference method. Other methods used in DEFRA networks include measurements of black smoke, particle number and size by condensation particle counters and Scanning Mobility Particle Sizers which provide complementary information which assists in understanding the sources and properties of airborne particles. Simple size fractionation into $PM_{2.5}$ and $PM_{2.5-10}$ fractions is helpful in understanding the sources of particles whilst measurement of full size distributions provides deeper insights into the sources of airborne particles. Whilst measurements of physical properties alone are useful, considerably further information is gained from measurement of chemical properties of airborne particles. Most studies to date have been concerned with measuring very small ranges of specific constituents which can be useful in evaluating particle sources, time trends and possible adverse effects of specific components. By compiling data from different studies it is possible to build a picture of the major component composition of particulate matter in the UK atmosphere but not to obtain mass closure, i.e. the ability to sum the individual components to equal the gravimetrically measured mass of particles. There have to date been no wholly comprehensive measurements of particle composition within the UK atmosphere and attempts at mass closure have needed to infer the mass of certain components. Whilst concentrations have been determined for large numbers of organic compounds in the atmosphere, these present only a relatively small proportion of the total mass of organic compounds and much remains to be learnt of the chemical nature and diversity of specific organic compounds in the atmosphere. Certain organic compounds are useful as atmospheric particle source tracers, but this aspect has not to date been exploited in the UK. One of the main policy applications of multi-component chemical composition data is in receptor modelling of airborne particulate matter in order to attribute the mass measured in the atmosphere to specific sources of emission. The models used have been steadily developing in complexity in order to provide a more reliable source attribution. Such information is critical to the development of effective mitigation strategies. In order to improve confidence in existing source apportionment models, the collection of comprehensive chemical composition information on airborne particles and the measurement of the composition of emissions from major source categories, together with the application of organic source tracers, would prove highly beneficial.

1. INTRODUCTION

This review has been prepared under the terms of a research contract (Reference CPEA 6) let by the Department for Environment, Food and Rural Affairs (DEFRA) and the devolved administrations for the purpose of characterising the chemical composition and sources of UK ambient particulate matter (PM) in order to inform air quality policy. The work is for a period of three years from January 2004 to December 2006.

The purpose of this document is to review recent scientific and technical issues with the aim of highlighting implications for policy.

The Quality of Urban Air Review Group (QUARG) published its third report in 1996 on issue of airborne particulate matter in the UK urban atmosphere. The report reviewed knowledge of sources, physical and chemical properties and concentrations of airborne particles in UK urban air, as well as the measurement methods. It reported emission inventories for primary particles and reviewed both measurements and model predictions for secondary particles. The receptor modelling techniques, based on the analysis of measurements rather than predictions from knowledge of emissions, was used for the source apportionment of particulate matter. Three predominant sources were identified as secondary inorganic sulphate and nitrate, vehicle exhaust emissions and suspended soils and road dusts. This method provided valuable estimates of the contributions from the two main controllable source categories, i.e. road traffic and secondary inorganic particles and allowed an approximate prediction of the impact of control strategies to be made.

The Airborne Particles Expert Group (APEG) published a report three years later on source apportionment of airborne particulate matter in the UK. It included new information following the third report of QUARG and provided more sophisticated methods for source apportionment to estimate the contributions from various source categories to the concentrations of airborne particulate matter in the United Kingdom and to make projections of contributions into the early part of this century.

Both the QUARG and the APEG reports were based on measurements which are now around 7-10, or more years old, and need to be updated. Also, knowledge of sources has been refined and new methods for source apportionment have emerged. This review has used the Third report of QUARG and the report of APEG as starting points, and conducted a search of relevant bibliographic databases for more recent studies, involving the characterisation (both chemical and physical) of particulate matter in the UK atmosphere. Whilst there are a number of studies with relevant information on a limited range of chemical components, these are not comprehensive studies and it will be necessary to synthesise information from different sources to provide a valid overview of what is known of the chemical make-up of airborne particles in the UK and of their particle size distribution. The current particle measurement methods and instrumentation are also outlined.

1.1 Structure of Report

The report is structured so as to present firstly a very brief review of the health effects of particulate matter and the air quality standards, guidelines and limit values designed to minimise the effects of human exposure. Subsequently, measurement methods are reviewed with a particular emphasis given to those methods used in the automatic urban and rural network. A review is then provided of the measurements of physical properties of airborne particulate matter in the UK atmosphere such as particle mass and number size distribution. Subsequently, measured chemical properties are discussed especially in the context of their use in source apportionment and mass closure. The final main section deals specifically with issues of source apportionment.

2. HEALTH EFFECTS AND LEGISLATION

The requirement to control atmospheric concentrations of particulate matter derives from its well recognised and quantified effects upon human health, including premature mortality, hospital admissions, allergic reactions, lung dysfunction and cardiovascular diseases. Currently, however, it is unclear as to which components or size fractions of airborne particles play the largest role in exerting the toxic effect. A discussion paper (Harrison and Yin, 2000), which considered information upon the composition and sizes of airborne particles in relation to exposure-response coefficients deriving from epidemiological studies in different parts of the world was unable to form any clear conclusion on the presence of dominant factors in the toxicity. However, a time series study (Laden et al., 2000), which used principal components of chemical characterised $PM_{2.5}$ particulate matter reflecting different source categories as its exposure metric, revealed a ranking of sources in exerting a toxic effect in the order: road traffic > coal combustion, > crustally-derived particles.

Many epidemiological studies have found a positive correlation between PM_{10} mass and respiratory illnesses and cardiovascular diseases (Dockery et al., 1993; Abbey et al., 1999). Other studies suggest that it is the finer particles, which have the greatest impact on health (Schwartz et al., 1996;

Cifuentes et al., 2000), which is supported by the fact that $PM_{2.5}$ penetrates the human respiratory system more efficiently into the alveolar region. Nevertheless, studies have also found that higher concentrations of coarse particles ($PM_{2.5-10}$) can also increase overall mortality rates (Castillejos et al., 2000). Miguel et al. (1999) suggested that re-suspended road dusts contain materials which can potentially initiate allergic reactions. Studies on both rodents and humans demonstrate that ultrafine particles have a greater effect per unit mass than larger particles (Oberdorster, 2001; Donaldson et al., 2000), while another study on asthma patients performed in Germany and Finland (Wichmann and Peters, 2000) suggested that both fine and ultrafine particles have health effects which might be independent of each other. Some studies have also shown that the chemical composition of the particles may mediate the health effects. A study in London showed that PM_{10} has the greatest effect on respiratory mortality (4% increase in deaths of all ages for a 10^{th}-90^{th}-percentile increment), while black smoke (fine particles of diesel origin) was associated with cardiovascular deaths (Bremner et al., 1999). Acidic particles may be irritant, PAHs (polycyclic aromatic hydrocarbons) potentially carcinogenic, and the trace metals delivered to the lungs on fine particles may catalyse production of tissue-damaging oxidants (Ghio et al., 1996; Dreher et al., 1997). Various species (sulphate, nitrate and black smoke) associated with the finer particles have been found to be associated with total mortality (Hoek et al., 2000), although the relationship may well not be causal.

The European Union limit value for PM_{10}, for which compliance should be reached by 2005, is 50 $\mu g\ m^{-3}$, as measured over 24 hour periods, which should not be exceeded more than 35 times per year. In addition the annual mean should not exceed 40 $\mu g\ m^{-3}$. Presumptive future limit values, for which compliance is required before 2010, are 50 $\mu g\ m^{-3}$ (to be exceeded no more than 7 times per year) and an annual mean of 20 $\mu g\ m^{-3}$. The CAFE (Clean Air for Europe) process within Europe, with very active participation from the United Kingdom, is currently deliberating upon appropriate metrics for regulating airborne particulate matter and it appears likely that a new limit value based upon the $PM_{2.5}$ metric will be recommended, but that monitoring of PM_{10} will also be required.

This project is concerned with determining the chemical composition of airborne particulate matter in the UK atmosphere within the size fractions PM_{10}, $PM_{2.5}$ and PM_1. Such information is of great value in developing policy on air quality in two distinct but inter-related areas. Currently, within the United Kingdom, monitoring of airborne particulate matter as PM_{10} mass is widespread, and knowledge of the range and spatial distribution of PM_{10} concentrations is generally good. In contrast, relatively few sites monitor $PM_{2.5}$ which has recently been highlighted by the World

Health Organisation review commissioned by CAFE as being the component of airborne particulate matter most closely associated with adverse health effects (although not the sole constituent responsible). Measurements of the size distribution of airborne particulate matter within the United Kingdom (Harrison et al., 2000) and other developed countries show a minimum in the mass size distribution at around 1 µm which separates particles from high temperature sources and gas-to-particle conversion processes (generally less than 1 µm diameter), from mechanically- generated particles such as soil, street dust and marine aerosol (which are generally greater than 1 µm diameter). There is therefore a need for monitoring $PM_{1.0}$ as well as, or instead of $PM_{2.5}$ in order to quantify those components with the strongest relationship to human activity, and possibly constituting a more toxic fraction per unit mass than $PM_{2.5}$ since the latter contains some particles from the mechanically generated fraction.

3. MEASUREMENT METHODS/TECHNIQUES

This section focuses especially on methods used in the Automatic Urban and Rural Network and other DEFRA networks. There are many other methods for measuring particulate matter, and a few of these are dealt with more briefly.

Sampling techniques for atmospheric particulates may be either (a) continuous or semi-continuous direct-reading instrumental methods, or (b) collection on filters followed by gravimetric determination. The latter procedure also allows for subsequent chemical analysis of the collected particles. In recent years traditional measurements of Total Suspended Particulates (TSP), which were determined typically by high volume filtration and gravimetric quantification of the mass of collected particles, have been replaced by more sophisticated procedures for quantification of the more health-relevant PM_{10} and $PM_{2.5}$ fractions.

3.1 The European Reference Method for PM_{10}

The European Reference Method for gravimetric determination of PM_{10} is defined in the standard method prEN12341. The version of the method used in the UK employs the low Kleinfiltergrat (KFG) sampler which draws air at 2.3 $m^3\ h^{-1}$ through a quartz fibre filter paper. The automated instrument accommodates a number of separate filters for sequential 24-hour periods which are held in external pods. Upon cessation of sampling, the filters are removed to the laboratory for weighing at a relative humidity of 50 ± 5% and a temperature of 20ºC ± 1ºC. The method is potentially subject to both positive artefacts by reaction of trace gases with the filter or on particles upon the filter and negative artefacts due to evaporative loss of semi-volatile components.

3.2 Methods Used in the Automatic Urban and Rural Network

Partisol

The R & P Partisol instrument collects particles at 16.7 L min^{-1} on an unheated filter after passage through a size selective inlet (PM_{10}, $PM_{2.5}$ or $PM_{1.0}$). In the dual-channel Partisol-Plus, after passing through a PM_{10} inlet the air-stream is split at a virtual impactor having a cut-off at 2.5 μm, so that a $PM_{2.5}$ fraction is collected at 15.0 L min^{-1} and a coarse fraction (comprising all particles >2.5 μm plus a smaller component of $PM_{2.5}$) at 1.7 L min^{-1}, onto separate filters. The instrument is fitted with an automated cartridge change-over facility and programming options to allow flexibility in collection times and intervals. The Partisol is similar in principle to the KFG, except that filters are contained within the instrument and maintained at a temperature within 5ºC of ambient.

Filters

The different types of filter available for air sampling were reviewed by Lodge (1993). Glass fibre filters have frequently been used with high volume samplers, however more recently PTFE (Teflon) filters have been used in low volume sampling applications due to their chemical inertness and low background levels of many analytes. The current EU specified reference method for monitoring PM_{10} requires the use of filters for gravimetric measurements. The filter weighing must be performed using an analytical balance with accuracy to within 10 μg (BSE, 1998), and equilibration must take place at a mean temperature of $20\pm1^{o}C$ and a relative humidity of 50±5 % over 24 hours.

Precautions are needed to avoid mechanical losses from filters post-collection. Thurston and Spengler (1985) demonstrated that loss of coarse particles could occur from filters during shipment from the field to laboratory. The coarse particle mass of shipped samples was on average 30-35% less than for samples transported by hand. Another study revealed that repeated dropping of packaged Teflon filter trays resulted in coarse particle mass losses of 10-53% (Dzubay and Barbour, 1983). No such effect was found for fine mass samples (Thurston, 1983).

Three major sampling methods or filter types have been used in Europe for collection of nitrate aerosols (Schaap et al., 2002). Those are 1) Denuder filter (DF) pack – the most reliable method to collect the semi-volatile nitrate by stabilising it after collection against evaporation, with very minor artefacts, 2) Inert filters (IF) – filters are made with chemically inert materials (Teflon and quartz) and give lower concentrations due to their largest artefact associated, the evaporation of ammonium nitrate and 3) Total nitrate (TN) filters – Impregnated filters, filter packs, nylon filters and cellulose filters all collect both nitrate and gaseous nitric acid, which needs to be corrected for. A potential artefact is the absorption of nitrous acid but this is usually negligibly small.

TEOM

The Rupprecht and Patashnick Tapered Element Oscillating Microbalance measures changes in the oscillation frequency of a tapered glass hollow tube due to the deposition of particles on a filter located at the upstream end of the tube. Air is drawn into the instrument via a PM_{10} inlet at 16.7 L min^{-1} with the airflow subsequently split with 3.0 L min^{-1} passing through the Pallflex 16 mm Teflon-coated glass fibre filter. Internal parts of the instrument are maintained at 50 ^{o}C to avoid condensation-induced errors. However at this temperature some loss of semi-volatile species such as ammonium nitrate and organic compounds may occur, leading to a difference of 15-30 % relative to a co-located gravimetric filter technique (where the filter is maintained at ambient temperature) (APEG, 1999). There is therefore a need for caution in interpretation, and particularly in prediction of the secondary material component, of TEOM data. In the UK, PM_{10} is mostly measured continuously using automated TEOM instruments.

Comparison was made for PM_{10} between a personal sampling head and the TEOM at AUN sites in Edinburgh and Belfast (Soutar et al., 1999). A significant linear relationship was found between the two types of monitor, with consistently higher concentrations from the PM_{10} head than from the TEOM. The results of regression analysis for the PM_{10} head versus the TEOM over summer, winter and the whole study periods are shown in Table 3.1.

Table 3.1 Results of regression of personal sampler versus TEOM for PM_{10}

Season	R	R^2	Regression equation	P value
Whole period (n = 43)	0.93	0.86	PM_{10} = 1.5 x TEOM + 5.9	<0.001
Summer (n = 23)	0.92	0.85	PM_{10} = 1.6 x TEOM - 0.5	<0.001
Winter (n = 20)	0.96	0.91	PM_{10} = 1.5 x TEOM + 11.2	<0.001

Salter and Parsons (1999) compared a TEOM Series 1400a with a Partisol 2000 at a location affected by emissions of crustal material (a china clay mining area of Cornwall, UK), and found a non-linear relationship described by $[\text{Partisol}] = 0.6989[\text{TEOM}]^{1.179}$, indicating that the differences between the two instruments are increasing when the PM_{10} concentrations are higher. A TEOM and a Partisol sampler are also co-located at Marylebone Road, London for PM_{10} measurement from June 1997 to January 2000 to test the suitability of a single correction factor applied to the TEOM PM_{10} data, which could then be used for assessing the EU Stage 1 PM_{10} limit, and the results indicated that a single correction factor will not reflect the site and season specificity (Green et al., 2001). Whilst the underestimation of PM_{10} mass by TEOM has been attributed to heating of the aerosol, a study of used TEOM filters from Swansea, Cardiff and Pembroke using high-resolution field emission scanning electron microscopy has found calcium sulphate crystals in spring and summer periods, and well-formed NaCl crystals throughout the year, and suggest that the internal heating system of the TEOM is not totally 'driving off' moisture as designed, which could challenge the reliability of the TEOM real-time weight recordings, if at times the weight was partially composed of water (Jones et al., 2001).

A sample equilibration system (SES) employing a Nafion drier has been developed for the TEOM, allowing collection at a lower temperature (30^{o}C) and hence reduced losses of volatiles (Meyer et al., 2000). A technique has also been developed at Brigham Young University in the U.S. for real-time measurement of aerosol mass including semi-volatile species (organics and ammonium nitrate), which combines a TEOM containing a quartz fibre filter impregnated with activated charcoal with a denuder in the inlet stream (the RAMS system). Volatile species in incoming air are removed by the (charcoal-coated) denuder to prevent positive artefact, and evaporating species in the TEOM are immediately scavenged by the filter media, preventing any losses from the filter itself (Eatough et al., 1999, 2001). PM_{10} measurement has been made at a kerbside in Sunderland in the northeast of England over the period from November 2000 to August 2001 using the new developed TEOM plus SES drier operating at 30^{o}C, a traditional TEOM series 1400 operating at 50^{o}C and a Partisol Plus 2025 air sampler (Price et al., 2003). The results suggest that the loss of semi-volatile organics and nitrates may not be the major cause of the observed differences between the monitors, and it is likely that the particle bound water in the Partisol data is responsible. The study concludes that it is difficult to apply a single factor to the TEOM data to make it comparable to data collected by the EU gravimetric method because the amounts of moisture associated with particles depends on the chemical composition and the ambient relative humidity and both factors vary spatially and temporally.

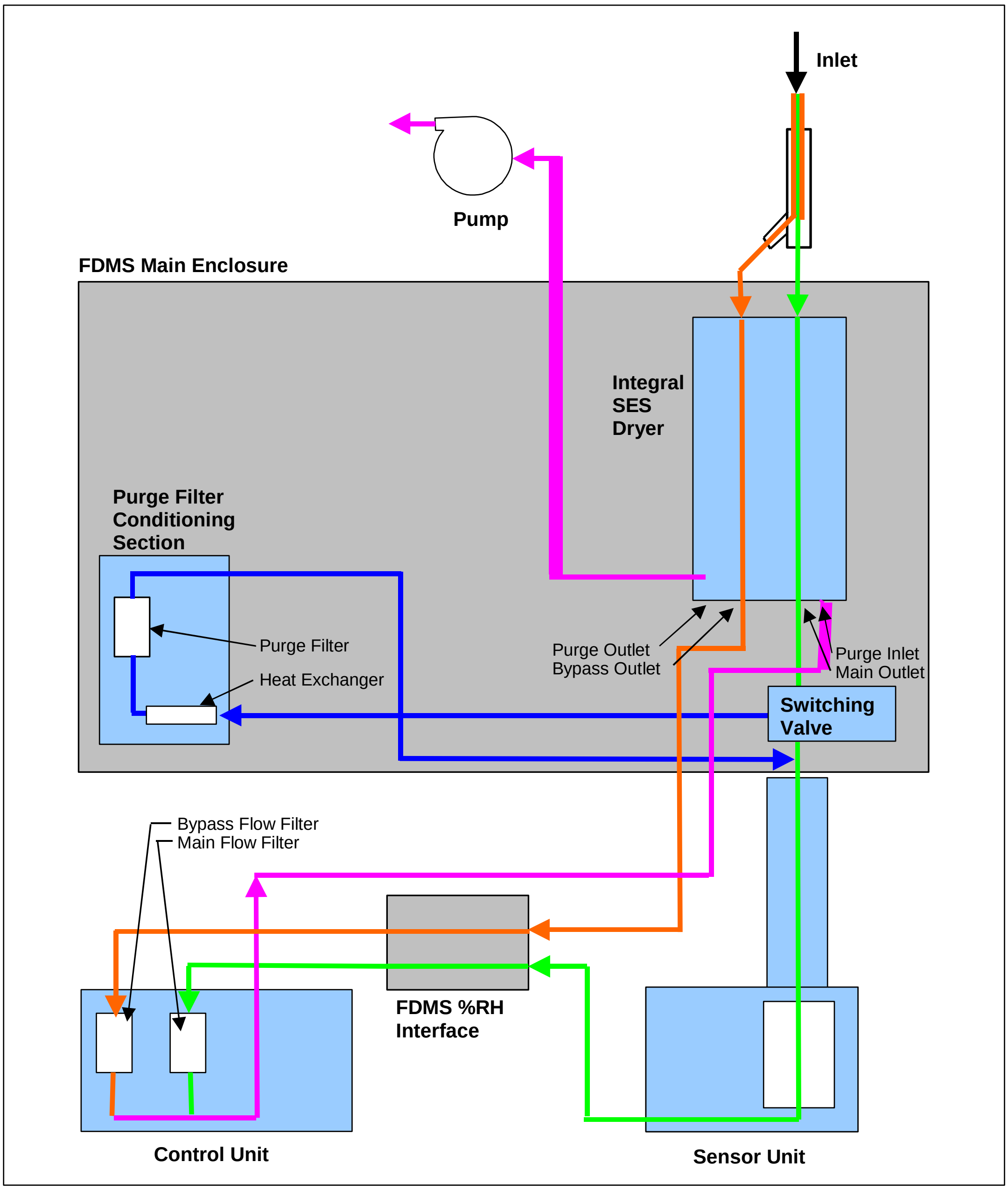
DEFRA has funded a preliminary intercomparison study including KFG, Partisol and unmodified TEOM instruments. Results are available at http://www.airquality.co.uk/archive/reports/cat13/0406301532_Intercomparison_report_FINAL.pdf In summary, the study revealed that the TEOM loses a substantial proportion of mass compared to the KFG and Partisol instruments but that the losses are sensitive to the locality (and hence the composition of particles and the season). Whilst at some sites such as Port Talbot, the divergence between the TEOM and gravimetric instruments was relatively small, at other sites with a higher proportion of semi-volatile material, losses were much greater. Unfortunately, due to day-to-day variability in particle composition there tends to be a considerable scatter in the relationships between gravimetric instrument measurements (i.e. Partisol and KFG) and the TEOM rendering the use of any simply correction factors impracticable.

With the intention of minimising this problem, the manufacturers of the TEOM have developed a correction system referred to as a filter dynamics measurement system (FDMS). The FDMS system is composed of two major sub-systems

- the sampling system consists of a size-selective inlet, flow splitter, air chiller/dryer and a switching valve that is used to direct the sample flow through the FDMS module;
- the analysis and control system which is made up of a sample filter that is part of the TEOM microbalance, humidity system for the main and by-pass flows and a control unit containing flow controllers and data management hardware.

A switching valve alternates the flow through the sensor unit between the sampler and purge flows every six minutes. After passing through the size-selective inlet, air is dried in an SES dryer (see above) and in the first six minute sequence passes through the normal TEOM sensor unit allowing determination of PM_{10} mass. In the next six minute period, the inlet air is diverted first through a purge filter maintained at 4ºC and the gases passing through that filter pass subsequently through the sensor unit and any loss of mass in the sensor unit filter is then used to correct the earlier reading of mass for evaporation of semi-volatile components. This is shown schematically in Figure 3.1. DEFRA has recently commissioned a detailed intercomparison study in which the performance of the standard TEOM, the TEOM/FDMS and that of beta-attenuation instruments is compared with the gravimetric reference method. Results will be available towards the end of 2005 or early 2006.

Figure 3.1: Schematic diagram of TEOM FDMS system



3.3 Methods Used in Other DEFRA Networks

Black Smoke

The British Standard method (OECD, 1964; BS1747, 1969) for measurement of black smoke involves collection of smoke particles by passage of the air-stream through a filter paper, which is subsequently analysed using a reflectometer. This is normally accompanied by the measurement of SO_2 by passage of the particle-free air-stream through a solution of hydrogen peroxide in a bubbler, with subsequent titration of the acidity produced. The equivalent particle mass is estimated using a Standard Smoke Curve. This technique does not yield accurate measurements of particulate mass since it relies on the presence of dark particles, which may only represent a fraction of the total mass (typically < 30%).

Condensation Particle Counters and Scanning Mobility Particle Sizers

Condensation particle counters are used to determine total particle number concentrations. The TSI model 3025A can count particles of sizes >3 nm, and the model 3022A particles >7 nm. Particles are grown to larger sizes by condensation of supersaturated vapour (butanol), then counted using an optical laser detector. The incoming aerosol passes over a heated wick soaked in butanol, and into a vertical condenser, which is maintained at a lower temperature using a thermoelectric cooler. The butanol vapour becomes supersaturated and condenses onto the aerosol particles. The resultant large particles enter the sensor, where a laser diode and lens system generate a light ribbon 10 μm x 2 mm. Light scattered by the particles is then focussed onto a photodiode, generating electrical pulses. For sample concentrations <1000 cm^{-3} all individual pulses are counted, in real time. Between 1000 – 10,000 cm^{-3}, individual pulses are counted only in "live-time", when the processing electronics are available, which corrects for particle coincidence. Above 10,000 cm^{-3}, the total light scattered by all particles present is measured. The maximum detectable concentration is 10^7 cm^{-3} (Model 3022A) and 10^5 cm^{-3} (Model 3025A).

The Scanning Mobility Particle Sizer (TSI Model 3934) comprises an electrostatic aerosol size classifier linked to a condensation particle counter. Aerosol particles entering the classifier are modified with a known charge using a radioactive ^{85}Kr source of β particles (which induce production of bipolar ions in air) and then enter an electrical differential mobility analyzer. This consists of two concentric metal cylinders, with airflows, (a) polydisperse aerosol and (b) sheath air, flowing laminarly down the annular space between the cylinders. The aerosol flow surrounds the sheath air inner core, and the inner cylinder (the collector) is maintained at a controlled negative voltage, creating an electric field between the cylinders. The voltage is varied such that particles in a narrow range of electrical mobilities (monodisperse) exit the classifier through a small slit at the base of the collector rod, with all remaining particles being removed in the excess airflow. Monodisperse particles leaving the classifier are counted using the condensation particle counter.

Urban particle number concentrations may be a useful indicator of road traffic emissions (Harrison et al., 1999). Scanning Mobility Particle Sizer measurements in Birmingham showed that the size distribution at the roadside possessed an additional mode at <10 nm, and particle number concentration was well correlated with PM_{10} mass.

Currently, DEFRA are supporting the operation of seven condensation particle counters and three Scanning Mobility Particle Sizers at carefully selected locations around the United Kingdom.

3.4 Other Methods not Currently Used in DEFRA Networks

Optical particle counters

Particles are sized and counted by detection of the amount of laser light (usually from a HeNe source) scattered from each particle. An example of this type of detector is the Particle Measuring Systems LASAIR particle counter, which determines the aerosol particle size distribution in up to 8 channels for particle diameters (μm) 0.1-0.2; 0.2-0.3; 0.3-0.4; 0.4-0.5; 0.5-0.7; 0.7-1.0; 1.0-2.0; >2.0. In the optical chamber a mirror-coated quartz crystal (part of an oscillator circuit) vibrates, shifting the wavelength of reflected light from a coupler mirror and maximizing power transfer into an external passive cavity. Collecting optics transfer scattered light to a photodiode detector, and the amplified signal is proportional to the size of the particle.

An example of portable instruments, the Grimm Labortechnik Portable Dust Monitor measures aerosol mass and size distributions in the concentration range 1 – 100 μg m^{-3} with a minimum measurable particle size of 0.75 μm. Measurement is based on angular dispersion or scattering resulting from passage of the poly-disperse aerosol stream through a light beam emitted by a laser diode. Scattered light is collected at a 90^o angle by a photo diode, and the amplified signal transmitted to an 8-channel pulse height analyzer for classification. Particles leaving the detector are collected on a final filter, used for gravimetric and/or chemical analysis.

Aerosol Time of Flight Mass Spectrometers

The Aerosol Time of Flight Mass Spectrometer (ATOFMS) is used to determine single particle size and chemical composition within the size rang 0.3-3 μm diameter. In these devices particles are accelerated through a nozzle, then collimated using successive skimmers, which allow removal of diverging particles. The remaining particles pass through a sequence of two laser beams, which allows calculation of particle velocity, and into the vacuum chamber. A de-sorption laser is timed to intercept the particle, the ions generated passing into a mass spectrometer and producing spectra characteristic of the particle. This equipment can be used for characterisation of non-exhaust particles from road traffic.

Integrating Samplers

Several other devices collect particles for subsequent gravimetric analysis. The Graseby Andersen PM_{10} High Volume Sampler (Hi-Vol) collects particles via a PM_{10} inlet onto unheated glass fibre or quartz filters at a flow rate of 1200 L min^{-1}. The GA dichotomous sampler collects at a flow rate of 16.7 L min^{-1} and separates the aerosol into fine and coarse fractions after sequential passage through a PM_{10} inlet and $PM_{2.5}$ virtual impactor. The EnviroTechnology MiniVol is a battery-powered portable device, which collects at 5 L min^{-1} through a PM_{10} inlet (un-validated) onto an unheated 47 mm filter. The Rupprecht and Patashnick ACCU sampler collects aerosol from the TEOM bypass line at 13.7 L min^{-1} onto a set of eight 47 mm filter cartridges.

Impactors

Impactors are multi-stage devices designed to separate the aerosol into aerodynamic size classes using their inertial properties. As an air-stream is drawn through an impactor the streamlines deviate, flowing around successive impaction surfaces. Particles with high inertia are unable to follow the streamlines, escape from the flow and impact onto the surface, while particles with lower inertia continue through successive stages. Subsequent stages possess progressively smaller jets (or slots) through which the air-stream is accelerated, so that increasingly smaller particles are provided with sufficient inertia to escape from the streamlines. The stage on which the particle impacts is determined by the combination of its inertial and aerodynamic properties, expressed as aerodynamic diameter. This is defined as the diameter of a unit density sphere, 1 g cm^{-3}, which settles at the same velocity as the particle concerned. Impactors such as the Berner low pressure impactor, the MSP Corporation Micro-Orifice Uniform Deposit Impactor (MOUDI), and the Andersen impactor collect aerosols in a range of particle size classes from around 50 nm to 20 μm. Sample collection times of 24 hours or greater are normally required to accumulate sufficient sample material for gravimetric or chemical analysis. Impactors may collect a higher mass when compared to the TEOM, a result of moisture or volatile organics collecting on the substrates, as well as losses from the heated TEOM sampler. Selection of suitable impactor substrates is therefore essential.

The Dekati Electrical Low Pressure Impactor (ELPI) is used to both provide real-time size distributions, and to collect samples for subsequent chemical analysis. The sample passes through a unipolar positive polarity charger where particles are electrically charged by ions generated using a corona discharge. The particles are then size classified according to their aerodynamic diameter in a low pressure impactor, where each individual stage is electrically insulated and connected to an electrometer current amplifier. The particles collected induce an electric current, the magnitude of which is dependent on the particle population. The current values are then converted to an aerodynamic size distribution using known properties of the charger and impactor stages.

4. PHYSICAL PROPERTIES OF AIRBORNE PARTICLES AND MEASUREMENTS WITHIN THE UK ATMOSPHERE

Airborne particulate matter represents a broad class of chemically and physically diverse substances, and consists of solid and liquid particles suspended in the air. It can be divided into primary particles emitted directly from sources such as vehicle exhaust and secondary particles formed in the atmosphere from condensation of vapours or by chemical reaction processes. Its size covers a wide range from a few nanometres to tens of micrometres, however only particles smaller than 10 micrometres in diameter are thought to have an adverse effect on human health. According to the current measurements, particulate matter can be classified as PM_{10} (50% cut-off aerodynamic diameters of 10 μm), $PM_{2.5}$ (fine particles, 50% cut-off diameters of 2.5μm), coarse particles ($PM_{2.5-10}$), $PM_{1.0}$ (50% cut-off diameters of 1.0μm) and ultrafine particles (diameter less than 0.1μm). Due to the mechanism of formation, particles are also classified roughly into three size modes, i.e., nucleation mode (0.01-0.1 μm), accumulation mode (0.1-2μm) and coarse mode (>2μm). Newly formed nucleation mode particles are very small about 1-2 nm in diameter, but rapid growth occurs to form larger particles by coagulation and condensation. The nucleation mode particles show a number mode of 20-30 nm in diameter. Particles in the accumulation mode will not grow further significantly through coagulation due to their low number concentration, have low rates of loss due to wet and dry deposition and therefore possess a longer atmospheric lifetime of several days and travel over very long distances within the atmosphere. The coarse mode particles have rather shorter atmospheric lifetime, especially particles larger than 10 μm.

Airborne particles are produced from a variety of sources, including incomplete combustion processes, industry and construction, as well as naturally as a result of re-suspension of surface soil material, sea spray, volcanic activity, biomass burning, organic debris and reactions leading to condensation of volatile precursors. Combustion emissions include directly generated carbonaceous material and trace elements, while hydrocarbons, SO_2 and NO_x released from natural and anthropogenic sources are oxidised within the atmosphere forming products which may either nucleate to form new particles, or be removed by condensation onto the surfaces of existing aerosols.

Fine and coarse particles possess distinct as well as similar mechanisms of formation, with a variable degree of source overlap. The former are often directly emitted as primary particles from combustion sources or formed by condensation of gaseous material through gas-particle conversion processes, or by condensation and adsorption processes (secondary particles). Fine particles are often derived from long-range transport, while coarse particles may be produced locally by mechanical attrition, disintegration processes (sea spray), industrial activities or re-suspension of surface material, particularly during drier conditions. In the UK urban areas, fine particles are dominated by vehicle exhaust emissions from road traffic and secondary particles, whereas coarse particles are less clearly defined, but major sources are re-suspended road dusts, windblown soils and sea spray particles (QUARG, 1996).

Particle Mass Measurement

Particulate mass concentrations vary greatly in time and space due to a wide diversity of geographical and meteorological conditions, as well as a variety of pollution sources. Available data on PM_{10} concentrations in the UK is mostly obtained from the Automatic Urban and Rural Network (AURN), containing mostly urban sites and only a few rural sites. Significant downward trends in the annual mean PM_{10} concentrations have been observed at most of the urban background sites from 1992/3 to 2000 (Stedman, 2002).

Since the summer of 1997, four additional sites have been set up to measure both PM_{10} and $PM_{2.5}$ continuously using TEOM, in London (one roadside, one urban background), Rochester (one rural) and Harwell (one rural), in addition to an older site at Birmingham, Hodge Hill (Harrison et al., 2001). A concentration summary for PM_{10}, $PM_{2.5}$, PM_{coarse} and NO_x is shown in Table 4.1. A significant concentration increment is observed at the roadside for both fine and coarse fractions. Generally, strong correlations between PM_{10} and $PM_{2.5}$ were found in all seasons. Coarse particle concentrations are generally higher in summer than in winter months, and higher also at urban than at rural sites. Coarse particle concentrations are also influenced by wind due to both dilution and resuspension effects, and the latter can increase the concentration but represent only a minor proportion of the total coarse fraction on larger timescales. Weekday-to-weekend and day-to-night differences between coarse particle concentrations are considerable at urban sites and appear to be due to anthropogenic activities. Strong correlations between both fine and coarse incremental particle concentrations (London roadside minus London background) and the incremental NO_x indicate the influence of both vehicle exhaust emissions and vehicle-induced resuspension. However, the data suggest that episodes of elevated coarse particle concentrations alone very rarely lead to exceedence of the UK air quality standard for PM_{10} of 50 $\mu g\ m^{-3}$ as 24-h running mean (Harrison et al., 1991).

Table 4.1. Summary of concentration data for PM_{10}, $PM_{2.5}$, PM_{coarse} and NO_x at all sites

	PM_{10} (μg m^{-3})	$PM_{2.5}$ (μg m^{-3})	Coarse (μg m^{-3})	NO_x (ppb)
Whole period				
LM (20/6/97-31/5/98	36.5	23.1	13.4	199.7
LB (20/6/97-31/9/98)	26.0	17.7	8.3	79.5
RO (20/6/97-31/5/98)	19.5	13.3	6.2	17.5
HAR (28/9/97-31/5/98)	16.8	12.2	4.5	21.4
HH (1/10/94-30/11/97)	22.5	14.5	8.0	53.5
Summer period				
LM (20/6/97-31/8/97)	40.7	26.4	14.3	187.9
LB (20/6/97-31/8/97)	27.3	18.9	8.4	63.8
RO (20/6/97-31/8/97)	22.3	14.2	8.1	12.9
HAR (20/6/97-31/8/97)	-	-	-	-
HH (1995-1997)	22.3	12.9	9.4	39.8
Autumn period				
LM (1/9/97-30/11/97)	37.7	23.3	14.3	221.7
LB (1/9/97-30/11/97)	29.4	19.3	10.1	109.1
RO (1/9/97-30/11/97)	19.1	13.2	5.9	22.0
HAR (28/9/97-30/11/97)	17.8	13.4	4.3	28.4
HH (1994-1997)	22.0	14.6	7.4	59.4
Winter period				
LM (1/12/97-28/2/98)	36.0	22.8	13.2	222.1
LB (1/12/97-28/2/98)	23.7	15.9	7.8	81.9
RO (1/12/97-28/2/98)	18.1	13.0	5.1	22.4
HAR (1/12/97-28/2/98)	16.6	12.0	4.5	18.7
HH (1994-19997)	21.1	14.6	6.5	62.5
Spring period				
LM (1/3/98-31/5/98)	31.8	20.0	11.8	167.1
LB (1/3/98-31/5/98)	23.7	16.8	6.9	63.2
RO (1/3/98-31/5/98)	18.8	13.0	5.8	12.9
HAR (1/3/98-31/5/98)	15.9	11.2	4.8	17.3
HH (1995-1997)	24.5	16.0	8.5	52.2

LM-London Marylebone Road; LB-London Bloomsbury; RO-Rochester; HAR-Harwell; HH-Hodge Hill, Birmingham; `—' indicates that data are not available.

Urban increments of ~15 μg m^{-3} were observed in urban areas of Leeds in comparison with a rural site, at where PM_{10} concentrations were on average 70% of those at urban sites (Clarke et al., 1999). PM_{10} was measured with a Partisol at three sites (one inner city kerbside, one outer city roadside and one rural) in Sunderland during a period from August 1997 to February 1998 (Price et al., 2003). Consistently higher PM_{10} concentrations were observed at the inner city kerbside site, with better inter-site correlation found in summer than in the winter period. Summertime exceedences of 50 μg m^{-3} are associated with conditions suitable for the build-up of photochemical pollutant, whereas exceedences in wintertime are recorded under a variety of weather conditions. $PM_{2.5}$ is also measured at the roadside site, which contribute 77% and 68% of the measured PM_{10} in summer and winter respectively. Measurements made in Birmingham in winter shows a higher $PM_{2.5}$ contribution ~80 % to PM_{10} mass, with strong correlation with NO_x showing that road traffic was a major source, while in the summer coarse particles mass (PM_{10}-$PM_{2.5}$) contributed ~50 % to PM_{10} mass and was correlated with windspeed. $PM_{2.5}$ comprised mainly vehicular emissions and secondary aerosols (Harrison et al., 1997).

PM_{10} levels in communities close to and away from opencast coal mining sites in Northeast England, were measured by Pless-Mulloli et al (2000) at five paired sites during 1996-1997 using a TEOM. Similar variations in PM_{10} concentrations were observed at all sites indicating regional influences. The arithmetic mean PM_{10} concentration in the opencast communities was 22.1 $\mu g\ m^{-3}$, which is about 14% higher than that in the control communities (PM_{10}: 18.2 $\mu g\ m^{-3}$). Fine and coarse particles from an urban street canyon in Nottingham were studied by Namdeo et al (1999) for a very short period in January 1998. 15-min averages showed no correlation between fine particles and traffic volume, but good correlation for coarse particles and traffic volume. Data at 6-second intervals suggests that both fine and coarse particle levels do not correspond with the variation of traffic flow. Measurements of PM_{10} and NO_2 at a canyon-street and a well-ventilated site in Cornwall indicate that roads with traffic flow considerably lower than 20,000 vpd (vehicle per day) can also raise the pollutant levels (Parsons and Salter, 2003).

Particle Number and Size Distribution Measurement

Particle number concentration is dominated by particles smaller than 0.1 μm (ultrafine particles), and the mass concentration is dominated by particles in the size range 0.1-0.5 μm (QUARG, 1996). On the other hand, ultrafine particles contribute very little to the overall particle mass concentration and nor do particles larger than 0.5 μm to the total particle number concentration. There are limited data about particle number and size distribution measurement in the literature and even less data available on a long-term basis. The majority of PM measurements based upon mass concentration cannot represent the variation of particle numbers.

Particle number and size distribution measurements were carried out in Birmingham at background and roadside sites during 1994-1995 (Harrison et al., 1999a&b) and 1996-1997 (Shi et al., 1999a) for only short periods. The average number counts were in the range 1.6-1.9 x 10^5 and 1.3-2.7 x 10^4 cm^{-3} at roadside and background locations respectively, indicating that particle number concentration is clearly affected by road traffic. The earlier study showed a more consistent single mode at about 30 nm for particle number size distribution at the background site, whereas the roadside presented far greater variation showing modes often at about 30 and below 10 nm or between 20 and 50 nm. Significant correlation was observed between particle number and mass concentrations, and particle count correlated better with $PM_{2.5}$ than with PM_{10}. Similar number modes were found (20-30 nm) in the later study. Those studies suggested that particle number is a better metric than PM_{10} for tracing vehicle exhaust emissions in an urban environment.

Measurements were also made in Birmingham during 1998 and 1999 for nanoparticles (< 10 nm) (Shi et al., 2001) at kerbside, roadside and background sites. The results indicate that road traffic is an important source of nanoparticles (3-7 nm), which contribute more than 36-44% of the total measured number concentration, and these nanoparticles are generated from both diesel and petrol fuelled vehicles. This is true also for sites within and proximal to an opencast coalmine in South Wales, at which vehicle exhaust emissions were found to be the largest source in terms of particle numbers (Jones et al., 2002).

Particle number size distribution data were obtained using an SMPS instrument, from the London Marylebone Road site over the period from April 1998 to August 2001 (Charron and Harrison, 2003). The data indicated that the particle number at the kerbside site was related to both vehicle emission intensity and meteorological parameters as well as pre-existing particle concentrations. The study revealed that the accumulation mode particles were associated with emissions from heavy-duty traffic (mainly diesel vehicles) whilst a stronger association was found between particles in the range 30-60 nm and light-duty traffic. There is no clear relationship between traffic volumes and particles in 11-30 nm range, but this fraction shows early morning peaks containing freshly nucleated particles, formed during the cooling and the dilution of semi-volatile gases from vehicle exhausts, inversely associated with air temperature. A dilution effect of higher windspeed was also observed on particles above 30 nm, but not on the smallest particle fraction (11-30 nm). On the other hand, rain seems to have a reversible effect on particle numbers for the size fraction smaller than 100 nm.

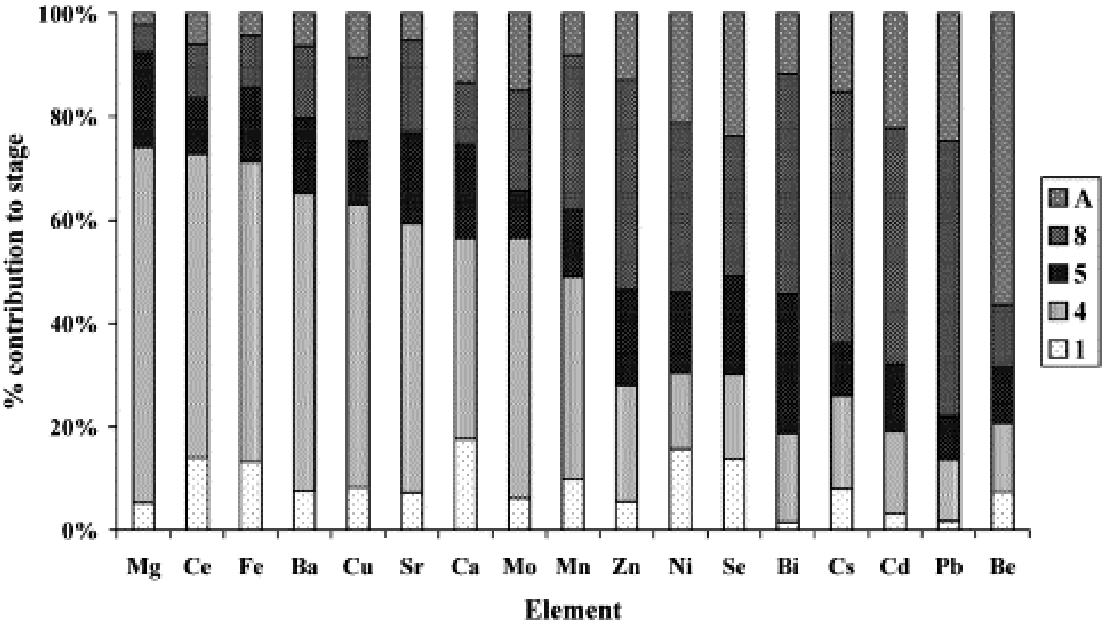
A 2-week measurement campaign of size-segregated aerosol (4.6nm-10μm) number concentrations in a typical street canyon in Manchester was conducted in October 2001 (Longley et al., 2003). The mean aerosol number size distribution observed showed a clear mode at 25-30 nm in diameter, consistent with the results obtained in Birmingham (Harrison et al., 1999; Shi et al., 1999), indicating a motor vehicle (particularly petrol) emission source. The mean roadside aerosol mass size distribution, estimated from the number concentration, exhibited two major modes: a fine mode ($D_p < 0.5$ μm) relating to the ultra-fine number mode, and a coarse mode ($D_p > 2$ μm). Coarse mode mass concentrations were generally found to follow urban background PM_{10} concentrations except with a 0-5 μg m^{-3} increment related to traffic-induced re-suspension of dusts. The wind direction, wind speed and traffic flow were found to have large effects on the aerosol number concentrations.

A combination of particle size distribution data from SMPS and APS instruments at a suburban site in Birmingham showed two distinct mass size modes, in the size range 0.1-1 μm and 1-10 μm respectively (Harrison et al., 2000), which suggests that monitoring $PM_{1.0}$ would be more logical than monitoring $PM_{2.5}$. Measurements at urban sites in Leeds using cascade impactors also indicated bimodality in the mass size distributions, but with slightly coarser modes at around 1 μm and 4-6 μm (Clarke et al., 1999). Typically 10-20% of the urban particle mass was within particles < 0.43 μm, with 50% in particles < 1.5 μm and 80% below 5 μm. The rural aerosol was depleted of mass in the <0.43 μm range, relative to the urban sites, due to a higher proportion of fine mode vehicular and industrial emissions in the urban area.

Detailed particle size distributions for specific chemical components are mostly measured with cascade impactors (e.g. MOUDI). Measurements in Leeds shows that nitrate was enhanced in coarser particles >2.1 μm and depleted in fine particles <0.65 μm, while ammonium was only found in fine particles in summer with a small fraction in winter in coarse particles. The size distribution of acidity (H^+) mirrored that of sulphate, and although the aerosols were normally well neutralised acidity was higher in fine and rural particles. Elemental carbon accounted for 17-27 % of PM_{10} in the urban environment, and 9 % at a rural site. No carbon was detected on the impactor back-up stage at the rural site, in contrast to urban sites, indicating redistribution (probably scavenging by larger particles) during transport away from source regions. 50 % of the elemental carbon was present in particles <0.6 μm, and 80 % in particles <3 μm.

The size distributions of particulate trace metals were studied at three background sites in central England and southern Scotland (Allen et al., 2001). The results identified three major behavioural types, including metals within the accumulation mode (Cd, Sn, Pb, Se), metals having multiple modes over fine, intermediate and coarse modes (Ni, Zn, Cu, Co, Mn, Hg), and those found mainly within coarse mode (Fe, Sr, Ba). The study was able to link size specified metals with emission sources of airborne particles, which are believed to include a) primary emissions of ultrafine particles from combustion and/or industrial processes, b) advection of air mass containing aged intermediate size aerosols and/or primary emissions of particles in this size range and c) large particles arising mainly from resuspension (such as Fe) or frictionally generated particles (mechanical wear). Another study on size distributions of trace metals in Birmingham has linked a number of elements with related emission sources of either natural or anthropogenic character (Figure 4.2) (Harrison et al., 2003). Fe, Cu, Mg, Sr, Mo, Ce and Ba are observed predominantly in the coarse fraction (2-10 µm), with very similar distributions for Mg, Ce and Fe. Ce and Fe appear to represent a crustal source whereas Mg probably originates in marine aerosol due to a strong correlation with chloride. Ca shows a greater fine particle component than the geochemically similar Ba, suggesting it to have both natural and anthropogenic origins, which is supported by the higher correlation between Ca and the diesel exhaust tracer, methylphenanthrenes, for finer size fractions. The only element with bimodality is Mn indicative of having both crustal and anthropogenic origins. Ni, Zn and Se show an even size distribution suggestive of having multiple sources. Bi, Cs, Cd and Pb are most abundant in the 0.2-1 µm and <0.2 µm size ranges.

Figure 4.2. Size distributions of the elements, in which stage A, <0.2 µm; stage 8, 0.2–1 µm; stage 5, 1–2 µm; stage 4, 2–10 µm and stage 1, >10 µm aerodynamic diameter.



5. CHEMICAL PROPERTIES OF AIRBORNE PARTICLES AND MEASUREMENTS WITHIN THE UK ATMOSPHERE

The chemical composition of PM is highly variable due to pollution sources, chemical reactions in the atmosphere, long-range transport effects and meteorological conditions. Components include neutral and highly water soluble substances such as $(NH_4)_2SO_4$, NH_4NO_3 and NaCl, through sooty particles composed of largely elemental carbon coated in organic compounds, and insoluble minerals such as particles of clay.

The relative abundance of the major chemical components, termed as ‘bulk chemical composition’ was reviewed in the studies of Harrison and Jones (1995) and Harrison and Yin (2000) for urban areas in the UK and around the world. These major components include carbonaceous compounds (elemental carbon and organic compound), secondary sulphate, nitrate and ammonium particles, sea salt, crustal materials or mineral dusts and biological materials. There were only two UK sites, Birmingham and Leeds, with extensive chemical composition data at the time. Substantial variation was found on the bulk chemical composition around the world at different locations even within one large country (e.g. in the eastern and western US). However in the UK the bulk chemical composition data from Leeds and Birmingham are very similar although they were measured at different times, i.e. in 1982 and 1995 respectively. In addition to the bulk composition, Harrison and Yin (2000) also discussed trace element and strong acid contents. The reviewed data does not show huge variations between major cities in the total trace element concentrations, but their speciation is particularly important regarding bio-availability and potential to influence human health. The strong acids nitric acid and sulphuric acid are formed in the atmosphere from oxidation of nitrogen dioxide and sulphur dioxide. Nitric acid vapour reacts with sea salt or ammonia to form sodium nitrate or ammonium nitrate respectively, whereas sulphuric acid is predominantly neutralised by ammonia to form ammonium bisulphate or ammonium sulphate (Harrison and Allen, 1990).

Sulphate is formed mainly through the oxidation of SO_2 in the atmosphere and is expected to be present mostly in the fine fraction as ammonium sulphate although some is present as sodium sulphate of marine origin. Sulphate aerosols may also be produced by reactions of dimethylsulphide (DMS) released into the atmosphere by marine biota, but concentrations over land arising from this source are small. The spatial gradient of sulphate is normally very small within areas of tens of miles (Burton et al., 1996), but over hundreds of miles it can be significant (QUARG, 1996). Concentrations of sulphate vary across Europe, and the highest levels, on an annual basis, occurred in a broad band extending from central England to central and southern Europe, with lower overall concentrations in western regions including Ireland and Scotland (Hjellbrekke et al., 1997). Annual mean concentrations of sulphate obtained from the European Monitoring and Evaluation Programme (EMEP) network in 1995 were 3.5-4.6 $\mu g\ m^{-3}$ in southern and eastern England, and 1.5-1.7 $\mu g\ m^{-3}$ in Ireland. Sulphate aerosols are ubiquitous in the atmosphere, with frequent periods of higher concentrations above background levels of around 0.5-1.2 $\mu g\ S\ m^{-3}$ in England and 0.3 $\mu g\ S\ m^{-3}$ in remote regions of Ireland and Scotland, and prevalence in fine particles (<2.5 μm) results in considerable spatial homogeneity over both urban and rural areas (e.g. Clarke et al, 1984).

Nitrate is formed mainly from the oxidation of NO_x. One major form is ammonium nitrate generated through the reaction between gaseous nitric acid and ammonia, which is a major component in the fine particle fraction. A more recent study in Leeds indicates a bimodal size distribution of nitrate (Clarke et al., 1999). The coarse mode nitrate mainly consists of sodium nitrate, generated by the reaction between gaseous nitric acid and sea salt (e.g. NaCl) particles. In some environments such as coastal areas, sodium nitrate may be predominant. Larger spatial variation is expected for nitrate in comparison with sulphate. Long term measurements at Harwell in central England have shown a progressive increase in aerosol nitrate levels, with mean concentrations rising from 1-2μg NO_3^- m^{-3} (1954) to 5-7 μg NO_3^- m^{-3} (1991). At present measurements of HNO_3 and particulate nitrate are conducted at two sites in the UK, and particulate nitrate at several EMEP stations (Hjellbrekke et al., 1997). The trend towards higher total nitrate levels is mostly related to the increasing road vehicle population, a major source of NO_x (QUARG, 1996). Recent measurement of PM_{10} particles at Harwell has found very high hourly nitrate concentrations mainly associated with easterly airmasses originated from the European continent and passing over central London (Yin, 2002). The UK network for sulphate and nitrate measurements showed a clear downward trend in the sulphate concentrations from 1992 to 2000, but no obvious trend in the nitrate (Table 5.1) (Stedman, 2002).

Table 5.1. UK network mean sulphate and nitrate concentrations for the years 1992–2000 (μg SO4 m^{-3}, μg NO3 m^{-3}) (from Stedman, 2002)

Year	Measured Sulphate	Measured Nitrate
1992	2.6	2.8
1993	2.9	3.0
1994	3.0	2.1
1995	2.9	2.2
1996	3.2	2.7
1997	2.5	2.6
1998	1.9	2.1
1999	1.7	2.0[a]
2000	1.6	2.0[b]

[a] Measurements from Eskdalemuir only are available for 1999, value scaled to be consistent with the average of Eskdalemuir and High Muffles data available for earlier years.
[b] No measurements available, assumed to be the same as in 1999.

Schaap et al (2002) reviewed the aerosol nitrate concentrations across the western Europe. The average particulate nitrate and total nitrate concentrations at sites across Europe over the period 1994-1997 are shown in Table 5.2. By using these nitrate data as the starting points, nitrate concentration mapping for the winter (October-March) period was achieved by Delaunay triangulation and subsequent linear interpolation of the point data. High nitrate concentrations exceeding 4 µg m^{-3} appeared in a large area ranging from southern England over continental western Europe into Poland, with a maximum in Switzerland over 6 µg m^{-3}. There is strong gradient from south to north, with nitrate concentrations ranging from 2.5 µg m^{-3} in southern Sweden to <0.5 µg m^{-3} in mid-Scandinavia.

Table 5.2. Overview of the average annual nitrate concentrations at the indicated sites and for the winter season (October–March) only (from Schaap et al., 2002).

Station	Code	Country	Method	Year		Winter		Reference
				$\mathrm{TNO_3}$	$\mathrm{aNO_3}$	$\mathrm{TNO_3}$	$\mathrm{aNO_3}$	
Kolummerwaard	KO	NL	DF	-	4.6		4.9	RIVM (1999)
Bilthoven	BI	NL	DF	-	5.0	-	5.4	RIVM (1999)
Vredepeel	VR	NL	DF	-	5.1	-	4.4	RIVM (1999)
De Zilk	DZ	NL	DF	-	4.2	-	4.6	RIVM (1999)
Wieringerwerf	WI	NL	DF	-	4.8	-	4.9	RIVM (1999)
Huijbergen	HU	NL	DF	-	4.0	-	3.9	RIVM (1999)
Muncheberg[a]	MU	DE	DF	-	3.2	-	4.7	Zimmerling et al. (2000)
Wallisellen	WA	CH	DF	-	4.7	-	7.1	Thöni et al., (2000)
Colchester[b]	CO	GB	DF	-	4.5	-	4.6	Chung (2000)
Melpitz	ME	DE	OF	-	4.1	-	5.4	This study
Kocetice	KO	CZ	IF	-	2.8	-	3.4	EMEP (2000)
Svratouch	SV	CZ	IF	-	2.1	-	2.1	EMEP (2000)
Keldsnor	KE	DK	TN	5.5	4.8	5.9	5.5	Frohn et al. (1998)
Anholt	AN	DK	TN	3.9	3.2	4.0	3.6	Frohn et al. (1998)
Tange	TA	DK	TN	4.4	3.7	4.8	4.4	Frohn et al. (1998)
Ulborg	UL	DK	TN	4.3	3.6	4.6	4.2	Frohn et al. (1998)
Fredriksborg	FR	DK	TN	4.0	3.3	4.5	4.1	Frohn et al. (1998)
Payerne	PA	CH	TN	5.3	4.7	6.7	6.4	EMEP (2000)
Eskdalemuir	ES	GB	TN	1.7	1.1	1.9	1.5	EMEP (2000)
High Muffles	HM	GB	TN	3.2	2.6	-	-	EMEP (2000)
Leba	LE	PL	TN	3	2.4	3.7	3.3	EMEP (2000)
Diabla Gora	DI	PL	TN	2.9	2.3	4.0	3.6	EMEP (2000)
Jarczew	JA	PL	TN	3.9	2.9	5.0	4.4	EMEP (2000)
Rucava	RU	LV	TN	3.3	2.7	3.7	3.3	EMEP (2000)
Birkenes	BI	NO	TN	1.2	0.8	1.1	0.9	EMEP (2000)
Skreadalen	SK	NO	TN	1.0	0.6	0.7	0.5	EMEP (2000)
Osen	OS	NO	TN	0.6	0.2	0.6	0.4	EMEP (2000)
Vavihill	VA	SE	TN	2.7	2.1	2.9	2.5	EMEP (2000)
Roervik	RO	SE	TN	2.7	2.1	2.8	2.4	EMEP (2000)
Aspvreten	AS	SE	TN	1.2	0.6	1.3	0.9	EMEP (2000)
Uto	UT	FI	TN	1.8	1.2	1.8	1.4	EMEP (2000)
Virolahti	VI	FI	TN	1.4	0.8	1.5	1.1	EMEP (2000)

[a] Data for Muncheberg are for 1995–1998.

[b] Data from Colchester originate from a shorter time series, see text.

Averages over the period 1994–1997 unless otherwise indicated. The codes by which the locations are identified in the figures are given in the second column. Where appropriate "total nitrate" concentrations are tabulated, as well as the aerosol nitrate concentrations after correction for nitric acid.

Methods/filter-types are indicated as: DF=denuder filter pack; IF=inert filter; and TN=total nitrate method (includes nitric acid)

Ammonium is formed in the neutralisation of sulphuric and nitric acids by atmospheric ammonia. Data from Leeds indicate that ammonium is mostly present in the fine fraction and very little or often zero is found in the coarse mode (Clarke et al., 1984; Clarke et al., 1999). While generally sulphate concentrations in western Europe have shown a decreasing trend in recent years ammonium levels have remained relatively constant, although showing shorter term correlation with sulphate, which may be due to a greater association of ammonium with other species, such as nitrate, in the aerosol.

Chloride rises mainly from primary emissions of sea salt and during the winter months road de-icing salt. These contribute mostly to the coarse particles. In the UK in the 1980s marine chloride accounted for around 40 – 80 % of total chloride (Willison et al., 1989), with non-marine chloride increasing in winter, particularly in urban areas, during cold dry weather. This results in a rural : urban aerosol chloride ratio of 0.7 or less. APEG (1999) assumed that 75% of aerosol chloride in the UK was of marine origin, and using a sea salt : chloride mass ratio of 1.816 estimated the sea salt component at 1-3 $\mu g\ m^{-3}$ in Leeds (an inland location) and at >5 $\mu g\ m^{-3}$ near the coast in Lancaster. Higher sea salt contributions occurred in winter than in summer. For the urban area of Leeds, 20 % of chloride was present in particles <1.2 μm, 50 % <3.2 μm, and 80 % <6.0 μm. Chloride may be also secondary in the form of ammonium chloride, which is in the fine mode and derived from the reaction of ammonia and hydrochloric acid vapour, emitted from combustion sources such as incinerators and power plants. Under normal atmospheric conditions, ammonium nitrate and ammonium chloride are unstable existing in a reversible phase equilibrium with the gaseous precursors, i.e., nitric acid, hydrochloric acid and ammonia. These equilibria are largely controlled by temperature and relative humidity. Dissociation of ammonium nitrate and ammonium chloride occurs at high temperature and low relative humidity. On the other hand, they are relatively stable under conditions of high relative humidity and low temperature (Allen et al., 1989) Reductions in emissions of hydrogen chloride in recent years have made ammonium nitrate formation unlikely, and little particulate chloride is likely to be present in this form nowadays.

Elemental carbon (EC) and organic carbon (OC) are major constituents of smoke from incomplete combustion processes, in urban areas mostly from road traffic. Elemental carbon, also termed as black carbon (BC), is responsible for the soiling characteristics of particles and possesses very good adsorptive properties, which may allow it to carry more harmful materials. Organic carbon is mostly produced from combustion processes as semi-volatile compounds or formed through atmospheric chemical reactions (Bowman et al., 1997). It normally represents about 60-80% of total carbon (Harrison and Jones, 1995), but the ratio depends upon location and season (Castro et al., 1999).

Atmospheric particulate carbon aerosol (organic and black carbon) was measured in several urban, rural and coastal areas in Europe, with a thermal-optical transmission method (Castro et al., 1999). Whilst the total carbonaceous aerosol concentrations are higher in urban than in rural and coastal locations, a relative enrichment in organic carbon (higher OC/BC ratio) in summer periods is observed suggesting an increased formation of secondary organic carbon due to gas/particle conversion of VOCs as a result of photochemical activity. Similar enrichment in organic carbon is found at rural and remote locations in comparison with urban areas. A clear minimum OC/BC ratio was found, which increases from 1.1 in larger cities to 1.5 in rural and remote sites, and this ratio may be used to estimate the amount of secondary organic carbon assuming that the ratio of primary OC/BC is constant in all samples. The calculation is performed from the equation below

$$\mathrm{OC_{sec}} = \mathrm{OC_{total}} - \left(\frac{OC}{BC}\right)_{\mathrm{minimum}} \mathrm{x\ BC}.$$

The relative amount of secondary organic carbon estimated ranges from 17% in Birmingham, in winter, to 78% on the Portuguese coast, in summer with oceanic air. Secondary organic carbon always contributes more than 50% to the total organic carbon aerosol in the summer period, with meteorological conditions favourable to the occurrence of photochemical activity.

Crustal materials, confined mainly to the coarse fraction (Harrison et al., 1997a) are soil and wind blown dusts. Their compositions and concentrations can vary greatly due to local geology, surface conditions and meteorology, as well as human activities, like traffic and construction etc.

Biological particles vary widely in size and morphology, and include pollens, spores, bacteria and viruses, as well as fragments of various kinds. Most pollen grains are larger than 10 μm, however mechanical disintegration of the grains can produce particles as small as 1 μm or less, which are detectable using biochemical assay procedures. Fungal spores are usually 5 μm or larger, so that they may contribute to the coarse fraction mass, with highest concentrations in the summer and autumn. Phillips (1997) found that fungal spores contributed 25 % of particles in the range 5-10 μm, and >50 % of particles >10 μm, measured in Birmingham during August 1997. In London, during the summer of 1996, the hourly mass concentration of fungal spores was in the range 0.2 – 8.4 μg m^{-3}, with a mean of 2.0 μg m^{-3}. Biological material contributed an average 5 % of PM_{10} mass, and up to 12 % on an hourly basis (APEG, 1999). Bacteria are ~1 μm diameter, and viruses a few tens of nanometres, so that both contribute to PM_{10} and $PM_{2.5}$. In terms of number distribution, the ratio of biological particles to total particles is around 0.1 considering the size range 0.4-10 μm (Matthias-Maser and Jaenicke, 1995), with a contribution of around 10 % to the mass of particles in the range 2.5 – 10 μm.

Multi-component Measurement Studies

Aerosol PM_{10} mass and its chemical components were measured on weekdays and weekends at a coastal urban area in Dundee (Qin and Oduyemi, 2003a). Low concentrations were observed (Table 5.3) with no clear differences between weekday and weekend samples. The influence of meteorological factors on concentrations of PM_{10} mass and its chemical composition is not immediately apparent, but analysis by comparing the contributions of wind aspects with wind direction frequencies identified some possible sources.

Table 5.3. Concentrations of PM_{10} mass and chemical species (µg m^{-3}) in sample collected in Dundee (Qin and Odayemi, 2003a)

	Mass	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	K^+	Cl^-	Na^+	Mg^{2+}	Pb	Ni	Zn	Cu
Min	5.00	0.422	0	0.080	0	0	0.079	0.070	0	0	0	0	0
Max	36.50	7.455	7.692	3.121	2.310	1.432	2.888	3.915	0.560	0.133	0.093	0.168	0.062
Average	12.20	2.154	1.107	0.670	0.779	0.110	0.980	0.127	0.127	0.021	0.025	0.028	0.024
SD*	6.00	1.543	1.261	0.602	0.526	0.185	0.672	0.132	0.132	0.038	0.025	0.030	0.014
DL	0.05				0.012			0.001	0.001	0.042	0.009	0.002	0.005
Precision (%)		23.5	13.5	5.2	0.9	9.0	11.3	0.5	0.5	7.8	14.3	2.4	19.1

The relative composition of fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) particles was studied at two very different UK sites: rural/coastal (Lizard Peninsula, Cornwall) and urban roadside (Central London), with image analysis using a Scanning Electron Microscope (SEM) (Moreno et al., 2003). The coarse fraction in London comprised mostly iron, carbon, nitrate, and silicate particles, with minor amounts of sulphate and chloride. In comparison the rural/coastal site contained much higher proportions of silicates and chlorides, and relatively low proportions of iron and carbon. For the fine fractions at both sites the largest contributor is carbonaceous compounds, followed by sulphates and nitrates, with low contributions from iron, silicates and chloride. A detailed characterisation of silicate particles has indicated an entirely different geology for the two sites. The electron-microscope method is unsuitable for characterising semi-volatile components, and hence these data are not comparable directly with those measured by bulk chemical methods.

Particulate trace metals have been studied at a number of locations in the UK atmosphere. Al, Fe, Mn, Ni, Co, Cr, V, Cu, Zn, Pb measurements were made on the UK mainland coastal rim of the north east Irish Sea, including two urban (Liverpool and Preston) and one rural (Lancaster) sites (Chester et al., 2000). The geometric average concentrations of these trace metals varied between the three locations, and are higher at the two urban sites than at the rural site (Table 5.4).

Table 5.4. Concentrations and EF_{crust} values for the NE Irish Sea coastal stations (from Chester et al., 2000)

Trace metal	Collection site					
	Liverpool (*n*=60)		Preston (*n*=90)		Lancaster (*n*=90)	
	Average	Range	Average	Range	Average	Range
(A) Geometric average concentrations and ranges (units, ng m^{-3} of air)						
Al	317	72-1367	365	91-743	210	101-586
Fe	340	64-1201	589	152-2275	159	65-486
Mn	8.4	2.5-43	21	4.2-109	4.4	0.40-31.5
Ni	3.0	0.81-12	16	3.0-134	3.7	1.1-12
Co	0.42	0.06-1.2	0.68	0.08-5.1	0.14	0.05-0.50
Cr	2.1	0.81-7.1	13	2.9-93	1.7	0.49-6.6
V	7.3	1.3-52	7.7	0.78-52	3.0	0.24-12
Cu	21	5.4-169	17	4.0-114	4.6	1.3-15
Zn	36	7.0-213	153	29-760	25	6.7-100
Pb	43	7.5-215	45	6.9-250	15	3.6-82.5
	Liverpool		Preston		Lancaster	
(B) Average EF_{crust} values, based on the geometric averages for the total populations – see text						
Al	1.0		1.0		1.0	
Fe	1.6		2.4		1.1	
Mn	2.3		5.0		1.8	
Ni	11		49		20	
Co	4.4		6.2		2.2	
Cr	5.5		30		6.7	
V	15		13		8.9	
Cu	95		66.5		31.5	
Zn	134		493		140	
Pb	904		822		476	

Trace metal concentrations obtained at sites in central England and southern Scotland are shown in Table 5.5 (Allen et al., 2001). The concentrations at the Auchencorth site were lower than those obtained at central England sites. The ratios calculated as [concentration in European air]/[concentration in maritime air] are in the range 1.03-6.66, suggesting that higher concentrations were associated with easterly European air masses. Ratios were also calculated for those particles collected only onto MOUDI stages 7-11, which best represented long-range transported aerosol, and the analytical results showed higher levels of all metals during an easterly air mass.

Table 5.5. Geometric mean concentrations and (in italics) geometric standard deviations according to location (ng m^{-3}) (from Allen et al., 2001)

Location	Mn	Ni	Cu	Zn	Cd	Sn	Hg	Pb	Fe	Co	Se	Sr	Ba
Castlemorton	1.7	1.3	1.1	11	0.14	0.27	0.12	7.9	78	0.060	1.1	0.71	1.0
	2.1	1.8	2.2	2.0	2.5	2.5	1.9	2.2	2.5	1.4	1.3	1.4	1.8
Brownfields	6.2	1.8	13	63	0.62	3.7	0.10	30	260	0.11	1.2	1.2	6.9
	1.6	1.3	1.8	1.8	1.7	2.1	1.4	1.6	1.3	1.4	1.4	1.7	1.4
Auchencorth	1.5	0.8	1.1	5.2	0.050	nd[a]	nd	10	nd	nd	nd	0.41	0.97
	1.2	1.3	1.2	1.2	1.1			1.9				1.0	1.5

Concentrations of particulate inorganic ions, trace metals and PAHs were measured during a winter period (26 October 2000 – 17 January 2001) at a Birmingham roadside site (Table 5.6). The particle mass concentrations were presented separately as PM$_{10}$, PM$_{2}$, PM$_{1}$ and PM$_{0.2}$ and showed that PM$_{2}$ and PM$_{1}$ account for a large proportion of PM$_{10}$ (68% and 52% on average) at this UK urban site. Enrichment factors calculated using Ce as the reference element indicate that the enrichment of most trace elements at roadside sites arises mainly from vehicle wear products rather than exhaust emissions, and therefore organic compounds may be better source tracers for exhaust emissions (Harrison et al., 2003a).

Table 5.6. Mean concentrations of specific components of roadside PM_{10} compared with rural aerosol (from Harrison et al., 2003a)-

Component	Roadside aerosol (this study)	(Rural aerosol (Allen et al. (2000)	
		Brownfields	Castlemorton
(a) Mean concentrations of specific components of roadside PM_{10} aerosol (this study) and rural aerosols (Allen et al., 2001)			
PM_{10} (µg m^{-3})	18.8		
$PM_{2.0}$ (µg m^{-3})	12.8		
$PM_{1.0}$ (µg m^{-3})	9.8		
$PM_{0.2}$ (µg m^{-3})	4.7		
Cl^- (µg m^{-3})	1.66		
NO_3^- (µg m^{-3})	0.78		
SO_4^{2-} (µg m^{-3})	1.42		
NH_4^+ (µg m^{-3})	0.53		
Ba (ng m^{-3})	13.3	1.2	7.3
Be (ng m^{-3})	0.05	n.d.	*n.d.*
Bi (ng m^{-3})	0.33	*n.d.*	*n.d.*
Ca (ng m^{-3})	76.1	*n.d.*	*n.d.*
Cd (ng m^{-3})	0.51	0.68	0.2
Ce (ng m^{-3})	0.14	*n.d.*	*n.d.*
Cs (ng m^{-3})	0.02	*n.d.*	*n.d.*
Cu (ng m^{-3})	12.0	14.6	1.4
Fe (ng m^{-3})	204	105	270
Mg (ng m^{-3})	157	*n.d.*	*n.d.*
Mn (ng m^{-3})	6.4	6.7	2.2
Mo (ng m^{-3})	0.9	*n.d.*	*n.d.*
Ni (ng m^{-3})	2.5	1.8	1.5
Pb (ng m^{-3})	27.4	32.9	10.2
Se (ng m^{-3})	1.8	1.1	1.3
Sr (ng m^{-3})	2.4	0.74	1.4
Zn (ng m^{-3})	29.9	71.0	12.8
Particle number (cm^{-3})	54397		
NO_x (ppb)	56.7		
(b) Mean concentrations of polycyclic aromatic hydrocarbons (sum of particulate plus vapour) (ng m^{-3})			
Acenaphthylene	14.18		
Acenaphthene	1.41		
Fluorene	9.14		
Phenanthrene	21.91		
3-Methylphenanthrene	3.94		
2-Methylphenanthrene	5.65		
9+1-Methylphenanthrene	4.33		
4,5-Dimethylphenanthrene	3.06		
Fluoranthene	8.29		
Anthracene	4.66		
Pyrene	7.66		
Benzo[a]anthracene	0.73		
Chrysene	1.24		
Benzo[*b*+*j*+*k*]fluoranthene	1.09		
Benzo[a]pyrene	0.44		
Retene	1.03		
Benzo[e]pyrene	0.57		
Indenol[*123,cd*]pyrene	0.69		
Benzo[ghi]perylene	1.42		
Dibenzo[*a*,*h*+*a*,*c*]anthracene	0.12		
Coronene	0.47		

Some specific particulate organic compounds have also been measured in the UK atmosphere. Short-chain (C_{10} –C_{13}) polychlorinated n-alkanes (PCA) were measured at a semi-rural location in Lancaster over a 12 month period in 1997/98 (Peters et al., 2000). Significant PCA levels have been found with a mean concentration of 320 ± 320 pg m^{-3}, mostly present in the gas phase, contributing 95% to the total PCAs. The composition of PCAs is dominated by hexa- and hepta-chlorinated congeners, with $C_{12}Cl_7H_{19}$ congeners accounting for roughly 20% of the total PCA content. The study suggests that PCAs can be a major component of the persistent organic pollutant (POP) burden of the atmosphere, which has the potential of undergoing long-range atmospheric transport processes.

Nitrated polycyclic aromatic hydrocarbons (nitro-PAH) have been measured in Birmingham, within a road tunnel and a Birmingham central site, which is valuable for identifying emission sources from combustion processes (Dimashki et al., 2000). Measured concentrations are in general broadly comparable with those measured within other major cities of the world. The road tunnel measurements included 9-nitroanthracene, 1-nitropyrene, 1-nitronaphthalene and 2-nitronaphthalene, while two extra species, 2-nitrofluoranthene and 7-nitrobenz[a]anthracene, were also detected at the central site (Tables 5.7 and 5.8). Nitronaphthalene was detected only in the vapour phase, whilst 1-nitropyrene, 2-nitrofluoranthene and 7-nitrobenz[a]anthracene were found only in the particle phase, whilst 9-nitroanthracene is present in both phases. Temporal trends of atmospheric PAH concentrations were also studied at an urban background and a city centre sites in Birmingham. It was found that the concentration levels have declined appreciably between 1992 and 1997 at the background site, but not at the city centre site (Dimashki et al., 2001).

Table 5.7. Concentrations of nitro-PAH measured in Queensway Road Tunnel (from Dimashki et al., 2000)

Compound	Mean (*n*=8) (ng m^{-3})	Range (ng m^{-3})
9-Nitroanthracene		
Particulate	0.36	0.23-0.56
Vapour	0.16	0.14-0.20
1-Nitrophyrene		
Particulate	0.56	0.44-0.69
Vapour	$<0.22\times10^{-4}$	$<0.22\times10^{-4}$
1-Nitronaphthalene		
Particulate	$<0.61\times10^{-4}$	$<0.61\times10^{-4}$
Vapour	1.59	0.56-2.12
2-Nitronaphthalene		
Particulate	$<1.4\times10^{-4}$	$<1.4\times10^{-4}$
Vapour	1.25	0.62-1.57

Table 5.8. Measurements of nitro-PAH in the atmosphere of Birmingham (Nov 1995-February 1996) (from Dimashki et al., 2000)

Compound	Particulate (ng^{-3}) Mean (n=25)	Range	Vapour (ng m^{-3}) Mean (n=5)	Range
1-Nitronaphthalene	$<0.61\times10^{-4}$		0.089	0.033-0.207
2-Nitronaphthalene	$<1.4\times10^{-4}$		0.067	0.027-0.176
9-Nitroanthracene	0.130	0.034-0.520	0.057	0.014-0.177
1-Nitropyrene	0.090	0.019-0.204	$<0.22\times10^{-4}$	
2-Nitrofluoranthene	0.221	0.046-0.586	$<0.21\times10^{-4}$	
7-Nitrobenz[a]anthracene	0.033	0.011-0.059	0.74×10^{-4}	

Total suspended particulate matter (TSP) was analysed at two sites in central London (St Paul's) and north London (Bounds Green) in 1995/6 for total organic carbon (TOC), particulate elemental carbon (PEC), 16 PAHs and 23 n-alkanes (Kendall et al., 2001). In general, higher concentrations of all species appeared at the central London site (Table 5.9), with seasonal variations indicating higher concentrations of combustion related compounds occurring in winter and autumn. The contribution of TOC (7-45%) to TSP was higher than that of PEC (1-13%). The dominant PAHs were the higher molecular weight compounds, B(ghi)P, BaA and Chrys, whereas the highest concentrations of n-alkane compounds were those between C_{21} and C_{29} (Table 5.10). Statistical analyses of the organic compound concentrations indicate that a dominant petroleum source is present at both sites, with a higher diesel component at the central London site, which also suffers a stronger anthropogenic (vehicular) influence.

Table 5.9. Total organic (TOC) and particulate elemental carbon (PEC) in TSP samples collected from the London aerosol (µg m^{-3}) (from Kendall et al., 2001)

	St Paul's		Bounds Green	
	TOC	PEC	TOC	PEC
Number of samples	34	34	35	34
Geometric mean	7.6	2.6	6.3	2.0
Standard deviation	3.0	0.7	2.5	0.8
Range	4.6-14.6	1.2-4.3	2.4-12.2	0.7-4.2
As a % of TSP	17.2	5.9	17.5	5.4

Table 5.10. Annual arithmetic mean concentrations (ng m^{-3}) of 16 monitored PAH compounds in TSP at selected sites in London. The range of values determined is shown in brackets (from Kendall et al., 2001)

Compound	Previous studies (Baek et al., 1991a)			This study			
	Exhibition Rd, 1985/1986 (*n*=23)	Exhibition Rd, 1987 (*n*=25)	1987 Rural (*n*=2)	Bounds Green, 1995/1996 (*n*=48)	St Paul's (*n*=48)	1995/1996	SP/BG ratio of annual averages
Naph	-	-	-	0.03 (*ND*-0.13)		0.04 (0.01-0.19)	1.30
Aceny	-	-	-	0.08 (*ND*-0.47)		0.13 (0.01-1.61)	1.65
Acen	-	-	-	0.05 (*ND*-0.35)		0.07 (*ND*-0.68)	1.34
Fl	-	-	-	0.16 (*ND*-1.62)		0.13 (0.01-0.61)	0.83
Phen	0.41 (0.13-1.26)	0.11 (0.02-0.24)	0.02 (*ND*-0.03)	0.15 (0.01-0.69)		0.22 (0.02-1.04)	1.44
Anthr	0.45 (0.13-1.84)	0.18 (0.02-0.45)	0.03 (*ND*-0.05)	0.09 (0.01-0.54)		0.12 (0.01-0.31)	1.31
Pyr	1.17 (0.06-3.95)	0.79 (0.06-2.23)	0.21 (0.16-0.26)	0.18 (0.01-0.77)		0.26 (0.06-1.15)	1.45
Fluor	1.66 (0.36-6.06)	0.81 (0.15-2.43)	0.21 (0.19-0.23)	0.06 (*ND*-0.41)		0.09 (*ND*-0.41)	1.49
Chrys	1.18 (0.21-3.87)	1.22 (0.29-4.65)	0.16 (0.13-0.19)	0.65 (0.02-6.15)		0.97 (0.09-3.52)	1.48
BaA	0.55 (0.05-1.80)	0.79 (0.22-2.39)	0.28 (0.16-0.39)	0.73 (0.03-6.44)		1.16 (0.12-5.37)	1.60
BbF	1.08 (0.25-3.10)	1.16 (0.57-3.37)	0.52 (0.45-0.58)	0.33 (*ND*-2.57)		0.63 (0.05-4.16)	1.91
BkF	0.51 (0.12-2.92)	0.68 (0.30-1.68)	0.21 (0.17-0.25)	0.36 (0.01-1.66)		0.59 (0.09-2.29)	1.63
BaP	0.99 (0.18-5.44)	1.44 (0.38-3.44)	0.43 (0.41-0.45)	0.27 (0.01-1.93)		0.55 (0.03-2.88)	2.07
1123cdP	0.99 (0.21-3.43)	1.57 (0.73-3.32)	0.54 (0.43-0.65)	0.20 (*ND*-1.82)		0.44 (*ND*-3.00)	2.28
BghiP	2.86 (0.71-10.01)	3.30 (1.52-6.63)	1.16 (0.89-1.42)	0.93 (*ND*-6.99)		1.78 (0.01-8.91)	1.91
DahA	0.13 (0.02-0.53)	0.12 (0.04-0.37)	0.05 (0.02-0.07)	0.01 (*ND*-0.13)		0.02 (*ND*-0.46)	3.23
∑PAH				4.27 (0.23-27.87)		7.24 (1.04-32.04)	1.70

The semi-volatile organic content of atmospheric particles and the associated vapour phase was measured at two urban sites (A - near a busy road, B - further away from the road) in Birmingham over the period from August 1999 to August 2000 (Harrad et al., 2003). The individual component concentrations are listed in Table 5.11, showing differences between site A and B due to greater traffic influence at site A, and appreciable biogenic input of n-alkanols and n-alkanes at the less-traffic influenced and more vegetated site B. The latter effect at site B appears greater in spring and summer months. Intersite differences in concentrations indicate that while local traffic is a predominant source for prtroleum biomarkers, the higher molecular weight PAH, mostly present in the particle phase, can arise from both regional and local sources. Some secondary compounds including dicarboxylic acids and oxygenated PAH like fluoren-9-one did not show significant intersite difference in concentrations.

Table 5.11. Comparison of average concentrations (sum of both phases) selected compounds at Sites A and B (roadside and urban background respectively) (from Harrad et al., 2003)

Compound	Average concentration$\pm\sigma_{n-1}$ m^{-3} at Site A (n=24)	Average concentration$\pm\sigma_{n-1}$ m^{-3} at Site B (n=24)	*p*-Value for paired *t*-test
n-Hexadecane	7.0±3.7	2.9±1.6	< 0.05
n-Tetratiacontane	0.34±0.45	1.6±2.2	< 0.05
17α,21β-Hopane	2.4±2.4	0.91±0.85	< 0.05
20R-5α,14β, 17β-Ergostane (a sterane)	0.53±0.39	0.13±0.12	< 0.05
Palmitic acid	1.36±11.9	16.9±18.1	> 0.05
Stearic acid	10.3±8.1	5.5±3.5	< 0.05
Oleic acid	1.1±0.51	0.65±0.33	< 0.05
Pnenanthrene	21.1±14.9	9.4±7.2	< 0.05
3-Methyl phenanthrene	3.9±2.3	1.3±0.57	< 0.05
Benzo[*ghi*]perylene	0.77±0.54	0.43±0.56	< 0.05
Fluoren-9-one	5.8±3.7	4.6±3.4	> 0.05
Glutaric acid	2.6±3.4	3.1±4.2	> 0.05

6. SOURCE APPORTIONMENT OF AIRBORNE PARTICULATE MATTER IN THE UK

The contribution of primary particles to the atmospheric particulate loading may be quantitatively estimated from consideration of emission source strengths and dispersion modelling. However assessment of the contributions of all sources including secondary particles requires a different approach. Receptor modelling identifies the major sources contributing to the total aerosol mass from atmospheric measurements and by consideration of the covariance between different measured parameters. The variable origins of atmospheric particulate matter complicate source apportionment since emissions from some of the sources (such as resuspension) are not well characterised, and the atmospheric lifetimes of the different size fractions vary leading to disparities in transport distances. In addition, the formation of secondary aerosols from precursor compounds is complex requiring the inclusion of detailed chemistry in models; this is fairly well established in the case of nitrates and sulphates, but not for the production of secondary organic aerosols from gaseous precursors.

Receptor modelling has been used to characterise particulate air pollutant sources and calculate each source contribution to a particular pollutant. There are two traditional main techniques based on chemical mass balance (CMB) and multivariate statistics. CMB uses both known profiles of source emissions and ambient data from the measuring site, whilst multivariate methods can identify sources from ambient measurements alone (e.g. TTFA – target transformation factor analysis, FA-MLR – factor analysis-multiple linear regression, and APFA – absolute principal factor analysis). These models have been widely used in source apportionment of aerosol pollutants (e.g. Gordon, 1998; Hopke, 1991; Harrison et al., 1997a; Chan et al., 1999; Fraser et al., 2003). Other simple models like MLR (multiple linear regression) (Turnbull and Harrison, 2000; Stedman et al., 2001) and chemical mass closure (Salma et al., 2001; Ho et al., 2003; Harrison et al., 2003) have also been used to calculate source contribution or chemical composition of pollutants.

Receptor Modelling

The Third Report of the Quality of Urban Air Review Group entitled Airborne Particulate Matter in the United Kingdom identified three major categories of airborne particulate matter representing the bulk of the mass of particles in the UK atmosphere (QUARG, 1996). These were primary combustion particles, arising within urban air predominantly from road traffic emissions, secondary particles, mainly sulphates and nitrates formed within the atmosphere from oxidation of sulphur and nitrogen oxides and other, mainly coarse particles (greater than 2.5 µm) arising from mechanically generated sources such as resuspension of soil and road dust and marine aerosol. The primary combustion component was quantified through its relationship to carbon monoxide and NO_x used as quantitative indicators of road traffic emissions. The secondary component was estimated through field measurement data of sulphates and nitrates in the atmosphere.

The Airborne Particles Expert Group (APEG, 1999) published a report on source apportionment and used a simple regression model developed by Stedman (1997) to estimate contributions of primary, secondary and coarse particles to PM_{10} mass using measured concentrations of PM_{10}, black smoke/NO_x and sulphate. The model is expressed as:

$$[\text{measured } PM_{10}] = A[\text{measured black smoke}/NO_x] + B[\text{measured sulphate}] + \text{Other}.$$

When the black smoke contribution to PM_{10} was subtracted from the total, the remaining [secondary + coarse particles] was shown to correlate with sulphate, which was hence used as the indicator for secondary aerosols. The intercept of the regression line calculated for [PM_{10} – black smoke] vs. [sulphate], at around 5 $\mu g\ m^{-3}$, gave an approximation of the fraction of PM_{10} associated with “other” (mainly coarse) particles. Mass concentrations of secondary aerosols, mainly comprising ammonium sulphates and nitrates, were found to be around two to three times the mass concentration of sulphate (SO_4^{2-}), depending on location and the relative amounts of nitrate and sulphate. At urban sites in the UK, the coefficient for black smoke (A) was spatially variable between 0.6 – 1.0 depending on site, due to the existence of different primary emissions sources, and the sulphate coefficient varied between 2.25 – 3.1.

APEG (1999) inferred that road traffic was a major source of primary particles, with additional contributions from industry and electricity generation; commercial and residential combustion; industry including construction, mining and quarrying. The contribution from road traffic increased in relative importance with decreasing particle size, and in many urban areas this source dominated the primary component. 75 % of the primary combustion component was assumed to arise from road transport, and forecast to decrease by 49 % (from 1996 levels) in 2005 and 63 % in 2010 (the remaining 25 % of primary combustion material was assumed to remain constant). The secondary component was predicted to reduce by 19 % in 2005 and 30 % in 2010, with the "other" component remaining constant. The latter will have significant positive impact on air quality, particularly in the vicinity of roads. The contribution of coarse particles resuspended from the road surface due to passage of vehicles was assumed to remain unaffected by any reduction in exhaust emissions (APEG, 1999).

Overall mean PM_{10} (as measured using the TEOM instrument which may underestimate true concentrations by ~10-30 %) was predicted to decrease from 28 $\mu g\ m^{-3}$ (1995 value) to 23 $\mu g\ m^{-3}$ (2005) in central London, and from 23 $\mu g\ m^{-3}$ to 19 $\mu g\ m^{-3}$ in central Birmingham, with the 99th percentile of daily average concentrations reducing from 80 $\mu g\ m^{-3}$ to 69 $\mu g\ m^{-3}$ (London) and from 77 $\mu g\ m^{-3}$ to 65 $\mu g\ m^{-3}$ (Birmingham). These reductions would not meet targets and, moreover, take no account of unusual events such as Bonfire Night festivities and long range Saharan dust transport which can significantly raise particulate concentrations periods of a few days. Secondary PM_{10} in the UK was predicted to reduce linearly to around 70 % in 2010 relative to 1996, while no major changes were anticipated for the “other”, mainly coarse, particle fraction.

PM_{10} components, including primary combustion, secondary and other, has been estimated using the above model at an urban background site in London (Bloomsbury) for the years of 1996, 1997 and 1998 (Stedman et al., 2001). The primary component used was NO_x, instead of Black Smoke. The results showed that secondary particle concentrations are decreasing, whereas the other component levels are not, and that the highest concentrations for primary particles occurred in 1997. Daily proportions of PM_{10} were also modelled for the three years, with comparison made between the modelled "other" component and the measured coarse particles ($PM_{2.5-10}$). Good agreement was found between the two, but the "other" component tended to overestimate the coarse particle contribution to PM_{10} by about 20%. More information about this component is needed for its quantification, such as chemical analysis of related tracers, including Na, Ca, Fe and Si. Annual mean, 90th percentile of daily mean and 99th percentile of 24-h running mean PM_{10} from 1993 to 2010 was projected using the model based on 1996, 1997 and 1998 data. A decreasing trend in the concentration was found, and measured levels fell within the range of the three predicted lines, however large differences were found between the projections based on different years.

Heal et al (2000) used gravimetric PM_{10}, black smoke (BS) and sulphate aerosol (SA) from the national networks in central Edinburgh to determine the trends in time of the contribution of different sources of particulate matter to total PM_{10}. The Stedman model was used to quantify the three major sources, primary combustion, secondary inorganic and other (mainly non-combustion primary coarse particles). Better correlation between PM_{10}-BS and SA was found in summer than in winter, reflecting the much greater photochemical generation of secondary aerosol in summer. For Edinburgh, there is evidence that the contribution of other secondary aerosol (presumably nitrate aerosol) has increased relative to SA from 1992 to 1997. No change was found in the contribution from other aerosol to PM_{10} during the study period.

The model developed for APEG by Stedman takes no direct account of the concentration of nitrate in the air. The weakness is becoming increasingly important as nitrate to sulphate ratios increase due to the relatively greater abatement of SO_2 than NO_x emissions. The omission of nitrate (which is assumed incorrectly to vary in a constant ratio to sulphate) was not a major weakness when PM_{10} mass data were derived from TEOM instruments which, if operated at 50ºC, volatilise a large proportion of the nitrate content of the particles. However, with measurement methods for compliance with European Directives now based firmly upon gravimetric techniques, which collect a large proportion of airborne nitrate, this omission is important. Also, work at the University of Birmingham funded by DEFRA indicates that nitrate concentrations are highly episodic and contribute substantially to exceedences of the 24-hour limit value for PM_{10}. The model takes no account of secondary organic aerosol formed from the oxidation of volatile organic compounds. This component derives mainly from long-range transport and is therefore very different from primary organic carbon, which arises largely from local emissions sources. The coarse particle fraction is an intercept in the regression model and therefore is treated as a constant in projecting future concentrations. Whilst such treatment may be justified in the context of marine aerosol, concentrations of coarse particles from road traffic sources (i.e. resuspension), industry (e.g. quarrying) and construction/demolition sources are very unlikely to be constant with time.

Turnbull and Harrison (2000) expanded the Stedman model and applied a four-component multi-linear regression model at four different coastal, rural and urban sites:

$$[PM_{10}] = [a(\text{Black Smoke})] + [b(NH_4NO_3 + (NH_4)_2SO_4)] + [c(NaCl)] + \text{Other}.$$

Black Smoke was used as a surrogate for primary combustion particles, and both sulphate and nitrate (assumed to be present in the form of ammonium salts) were used to represent secondary material. The remaining components were sea salt (sodium chloride) and “other” (mainly coarse particles). Overall mean contributions to PM_{10} at the different sites were 28-35 % (secondary), 20-57 % (primary combustion), 11-34 % (sodium chloride) and 3-21 % (coarse fraction). Seasonal variations were observed for primary and coarse particles, but not for secondary material, which was more dependent on air mass origin. Coarse particles were generated locally in urban areas and showed peaks in the summer, while black smoke and PAH were highest during the autumn or winter.

Decreasing trends in measured annual mean PM_{10} concentrations from 1992/3 to 2000 at three sites, London Bloomsbury, Belfast Centre and Bury Roadside, have been studied by Stedman (2002) using a combination of a regression model and site-specific projections. The first step of the study is to use the regression model (APEG, 1999; Stedman, 2001) to assign the TEOM measured PM_{10} concentration to primary, secondary and other (largely coarse) particles using measured NO_x and sulphate data in 1999 for non-roadside sites, London Bloomsbury and Belfast Centre, and for the Bury Roadside site an extra component was added in the model as roadside increment using the measured roadside increment of NO_x as a marker. The second step is to divide the primary PM_{10} concentrations further into contribution from individual source sectors for 1999, including primary point, primary traffic and primary stationary area sources calculated using the Gaussian plume dispersion model ADMS and the primary emission maps for 1999 from the National Atmospheric Emissions Inventory (NAEI). The final step is to project forwards and backwards in time to construct concentration trends from 1992 to 2000 based on the measured 1999 data.

Very good agreement has been found between the projected and the measured total PM_{10} concentrations for the years 1992-2000. The downward trends in the measured annual PM_{10} (reduced around 29-34%) are also seen in the projected values (Table 6.1), which largely due to the reduction of secondary particles at London Bloomsbury (40%), stationary sources at Belfast Centre (53%) and roadside traffic emissions at Bury Roadside (49%).

Table 6.1. Components of annual mean PM_{10} concentration in 1999 derived from the receptor model, and in 1992 derived from the receptor model projections (µg m^{-3}, TEOM) (from Stedman, 2002)

	London Bloomsbury 1999	London Bloomsbury 1992	Belfast Centre 1999	Belfast Centre 1992	Bury Roadside 1999	Bury Roadside 1992
Primary points	0.4	0.7	0.1	0.2	0.4	0.6
Primary stationary	2.5	4.0	6.0	10.5	1.4	2.2
Primary traffic	3.7	6.5	3.1	5.5	2.3	3.9
Secondary	8.2	12.0	3.9	5.7	6.2	9.0
Coarse	7.2	7.2	6.9	6.9	7.9	7.9
Roadside	-	-	-	-	6.0	10.7
All components	22.0[a]	30.4	20.0[a]	28.7	24.0[a]	34.2
Measured concentration	22	30	20	27	24	-

[a] The all components total and measured concentrations are identical for the 1999 base year of the receptor modelling.

Five aerosol sources were identified in Dundee using a receptor model (positive matrix factorisation) (Qin and Oduyemi, 2003b), including marine aerosol, secondary ammonium sulphate, secondary ammonium nitrate, soil and construction dust and incinerator and fuel oil burning emissions. Another important source, vehicular emission, unidentified by the receptor model, was also considered and its contribution to PM_{10} was estimated using an atmospheric dispersion model. In all, 67.5% of the PM_{10} mass is accounted for by these six sources, with contributions at 17.8%, 9.5%, 12.1%, 16.9%, 1.8% from sea salt, ammonium sulphate, ammonium nitrate, soil and construction dust, and fuel oil burning respectively.

Colvile et al (2003) used an atmospheric dispersion model to access exposure of road users (cyclists) to $PM_{2.5}$ in central London, based on calculation as $C_{total} = C_{road} + C_{city} + C_{imported}$, where C_{total} is the $PM_{2.5}$ concentration, and C_{road}, C_{city} and $C_{imported}$ represent three $PM_{2.5}$ component concentrations on-street due to "nearest road" emissions, from the rest of London outside the street canyons and from sources imported into London, mainly secondary particles respectively. The latter component concentrations used measured data rather than modelled. Clear underestimation of the modelled exposure in comparison with the measured $PM_{2.5}$ exposure is thought to be attributable to short-range transient variability in the aerosol concentration associated with traffic queuing, signal control, and plumes from individual vehicles. Nevertheless, the nearest road is identified as the dominant source of $PM_{2.5}$ exposure, and imported secondary component is the second important source.

Chemical Mass Closure

A key consideration regard to source apportionment methodology is to seek either directly or indirectly to account for the full measured mass of particles. The current UK source apportionment method does not seek to do this, as about one third of the mass of particles is represented by an intercept in the regression and is therefore not accounted for chemically at all.

A simple mass closure model has been used to construct aerosol PM_{10} and $PM_{2.5}$ chemical composition ambient measurements (Harrison et al., 2003). 24-hour particulate sulphate, nitrate, chloride, organic carbon, elemental carbon, iron and calcium data were obtained at four paired urban road and background sites in London and Birmingham during the period between April 2000 and January 2002. The sampling was conducted with dichotomous Partisol samplers, which allowed for subsequent fine and coarse particle chemical analyses. The model construction includes six major components, i.e., ammonium sulphate, ammonium nitrate/sodium nitrate, sodium chloride, elemental carbon, organic compounds and mineral dusts. The component marker elements or compound and conversion factors used are shown in Table 6.2, with consideration of the water contents associated with the hygroscopic species. Comparison has been made through linear regression of reconstructed mass upon gravimetric masses, and indicates that a 100% of the measured mass was accounted for with a high percentage of variance in 24h mass concentrations explained.

Table 6.2. Adjustment factors used in the mass closure model of Harrison et al. (2003b)

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

Table 6.3. Results of linear regression of reconstructed mass (y) upon gravimetric mass (x) using the mass closure model of Harrison et al. (2003b)

Determinand	Sites	Regression		R^2	n
		RMA regression	Forced through origin		
PM$_{10}$	Roadside	$y = 1.00x + 1.33$	$y = 1.02x$	0.92	97
PM$_{coarse}$	Roadside	$y = 1.00x + 0.19$	$y = 0.98x$	0.73	97
PM$_{2.5}$	Roadside	$y = 1.00x + 0.97$	$y = 1.03x$	0.93	97
PM$_{10}$	Background	$y = 0.99x + 2.50$	$y = 1.05x$	0.84	97
PM$_{coarse}$	Background	$y = 1.00x + 0.58$	$y - 1.01x$	0.61	97
PM$_{2.5}$	Background	$y = 1.01x + 1.52$	$y - 1.02x$	0.90	97
PM$_{10}$	Roadside increment	$y = 1.08x - 0.96$	$y = 1.07x$	0.79	97
PM$_{coarse}$	Roadside increment	$y = 0.99x - 0.11$	$y = 0.86x$	0.66	97
PM$_{2.5}$	Roadside increment	$y = 1.19x - 1.52$	$y = 1.01x$	0.72	97

The above mass closure procedure offers the potential for a far more sophisticated source apportionment model since it contains better features. These features include: a) it accounts separately for nitrates and sulphates, b) it accounts for both secondary and primary organic carbon, c) it accounts for the mass of marine aerosol, which is seasonally variable and d) it contains a chemical marker for resuspended particles thereby permitting future changes in concentrations of particles from this source to be considered.

Aerosol chemical mass closure analysis is also used in many other studies but mostly conducted as a simple comparison between the sum of all measured chemical component masses and the gravimetric PM mass. Usually a great number of chemical species are measured in order to have a higher mass closure. Maenhaut et al (2002a) reconstructed the PM$_{2.5}$ and PM$_{2.5-10}$ mass with nine aerosol types. Crustal matter, organic aerosol and nitrate were the major components in the coarse size fraction, whilst the dominant aerosol types in the fine fraction were organic aerosol, nitrate and sulphate. The nine chemical components explained 116% and 86% of the gravimetric PM mass for the coarse and fine fractions. Measurements made by MOUDI impactor allowed chemical mass closure calculation for both the supermicrometre and the submicrometre size range (Maenhaut et al., 2002b). The dominant components are organic and crustal matter in the supermicrometre size range, and organic aerosol and sulphate in the submicrometre fraction. On average, 74% of the gravimetric PM was accounted for by the aerosol types considered.

Work in North America (Cass, 1998) which has yet to be extended to Europe has focussed on the use of organic compounds as molecular markers of specific source categories of airborne particles, even giving the potential to discriminate between diesel and petrol-fuelled vehicles (Fraser et al., 2003). Whilst markers have been developed for a range of sources including some such as meat barbequeing which are not expected to be of major significance in UK cities, the method may usefully be applied to elucidating the relative importance of different combustion sources in contributing to primary combustion emissions. Thus, the ability for example to distinguish between road traffic, coal combustion and fuel oil combustion may prove valuable in source apportionment, particularly as the road traffic contribution reduces progressively with the introduction of stricter abatement measures.

Lim et al (1999) estimated the contribution of traffic to atmospheric concentrations of PAHs using a simple CO-PAH and NO_x-PAH linear regression at a heavily trafficked city centre site in Birmingham. On average 71% and 59% of 4-7 ring PAH respectively originated from traffic. Using B[e]P as an indicator, the contribution of traffic to concentrations of 4-7 ring PAH was estimated as 80-82% and 61-67% for the city centre and another urban background sites respectively. About 60-84% of total PAH from traffic emissions originated from diesel vehicles at the centre site when using ratios of the sum of methyl phenanthrenes to phenathreneas an indicator.

A further area of considerable uncertainty in emissions inventories and in the source apportionment of particulate matter in the atmosphere is estimation of airborne concentrations of non-exhaust particles generated by road traffic. These include sources of resuspension of particles from the road surface, direct emissions of brake dust from both pads and discs and tyre wear particles.

Currently, the most promising techniques for distinguishing between particles originating from these sources, and especially for distinguishing between resuspended road dust and windblown soil particles, are techniques based upon aerosol mass spectrometry. These are single particle techniques giving detailed chemical characterisation of individual particles which may be used to relate them to their source. Pilot work at the University of Birmingham, funded by DEFRA and EPSRC, using an Aerosol-Time-of-Flight Mass Spectrometer (ATOFMS) has shown distinct chemical differences between particles arising from these sources, and with further development work, should permit the quantitative attribution of particles to the individual source categories. A recent example of the application of this technique in North America is given by Pastor et al. (2003).

7. CONCLUSIONS

Whilst there have been a considerable number of high quality studies of specific aspects of the physical and chemical properties of airborne particles in the UK atmosphere, there has to date been no comprehensive intensive study. Such a study would be very resource-intensive, but if properly designed, might advance knowledge and understanding in ways which have not been possible through aggregating the results of smaller piecemeal studies.

A particular deficiency which relates not only to the UK but to all countries is that mass closure has not been achieved through chemical analysis. Ideally, it would be possible to determine the mass concentration of all of the individual components and sum them to a value identical to the gravimetrically measured particle mass. Only when this is achieved can there be confidence in source apportionment results used in the planning and implementation of mitigation measures. For a number of reasons connected with minor components, the uncertainties in the ratio of organic compound mass to organic carbon mass, and the current inability to measure directly the concentration of strongly bound water, it is not possible to achieve a directly measured mass closure. It is therefore necessary to develop simpler pragmatic models such as the APEG (Stedman) and Harrison et al. (2003) models. Whilst such models provide a valuable platform from which to evaluate the performance of mitigation measures, there are inevitable uncertainties which derive directly from the absence of a fully measured mass closure.

There are a number of specific uses of measurements of chemical and physical properties of airborne particles. In the policy context these can include the following:

- measurements of directly toxic species which themselves require regulation (e.g. trace metals);
- for use in epidemiological studies designed to elucidate which physical properties or chemical components of airborne particulate matter bear the greatest responsibility for its toxic effects; and
- for use in source apportionment in order to devise cost-effective abatement strategies.

It is only the last of these applications which requires comprehensive chemical information and ideally needs mass closure. Highly beneficial in this regard would be comprehensive measurements of the chemical composition of particulate matter from a range of important primary sources which could then be used in both deterministic (chemical mass balance) and stochastic receptor modelling methods in order to derive a comprehensive source apportionment of particulate matter in the UK atmosphere.

REFERENCES

Abbey D.E., Nishino N., McDonnell W.F., Burchette R.J., Knutsen S.F., Beeson W.L. and Yang J.X. (1999) Long-term inhalable particles and other air pollutants related to mortality in nonsmokers, *AM. J. Resp. Crit. Care Med.*, **159**, 373-382.

Allen A.G., Harrison R.M. and Erisman J.W. (1989) Field Measurements of the Dissociation of Ammonium Nitrate and Ammonium Chloride Aerosols, *Atmos. Environ.*, **23**, 1591-1599.

Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M. and Greenwood, J.C. (2001) Size distributions of trace metals in atmospheric aerosols in the United Kingdom, *Atmos. Environ.*, **35**, 4581-4591.

Anderson, H.R., Bremner, S.A., Atkinson, R.W., Harrison R.M. and Walters, S. (2001) Particulate matter and daily mortality and hospital admissions in the West Midlands conurbation of the United Kingdom: Associations with fine and coarse particles, Black Smoke and sulphate, *Occup. Environ., Med.*, **58**, 504-510.

APEG (1999). Report of the Airborne Particle Expert Group: Source Apportionment of Airborne Particulate Matter in the United Kingdom, Department of Environment, Transport and the Regions, UK.

Bowman, F.M., Odum, J.R., Seinfeld, J.H., Pandis, S.N. (1997) Mathematical model for gas-particle partitioning of secondary organic aerosols, *Atmos. Environ.*, **31**, 3921-3931.

Bremner, S.A., Anderson, H.R., Atkinson, R.W., McMichael, A.J., Strachan, D.P., Bland, J.M. and Bower, J.S. (1999). Short term associations between outdoor air pollution and mortality in London, 1992-4, *Occup. Environ. Med.*, **56**, 237-244.

Burton, R.M., Suh, H.H. and Koutrakis, P. (1996). Spatial variation in particulate concentrations within metropolitan Philadelphia, *Environ. Sci. Technol.* **30**, 400-407.

Castillejos M., Borja-Aburto V.H., Dockery D.W., Gold D.R. and Loomis D. (2000) Airborne coarse particles and mortality, *Inhal. Toxicol.*, **12**, 61-72.

Cass G.R. (1998) Organic molecular tracers for particulate air pollution sources, *Trends in Analytical Chemistry*, **17**, 356-366.

Castro, L.M., Pio, C.A., Harrison R.M. and Smith D.J.T. (1999) Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations, *Atmos. Environ.*, **33**, 2771-2781.

Chan Y.C., Simpson R.W., Mctainsh G.H., Vowles P.D., Cohen D.D., Bailey G.M. (1999) Source apportionment of $PM_{2.5}$ and PM_{10} aerosols in Brisbane (Australia) by receptor modelling, *Atmos. Environ.*, **33**, 3251-3268.

Charron A. and Harrison R.M. (2003) Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere, *Atmos. Environ.*, **37**, 4109-4119.

Chester R., Nimmo M., Fones G.R., Keyse S. and Zhang Z. (2000) Trace metal chemistry of particulate aerosols from the UK mainland coastal rim of the NE Irish sea, *Atmos. Environ.*, **34**, 949-958.

Cifuentes L.A., Vega J., Kopfer K. and Lava L.B. (2000) Effect of the fine fraction of particulate matter versus the coarse mass and other pollutants on daily mortality in santiago, Chile. *J. Air Waste Mgt. Assoc.*, **50**, 1287-1298.
Clarke A.G., Azadi-Boogar G.A. and Andrews G.E. (1999) Particle size and chemical composition of urban aerosols, *Sci. Tot. Environ.*, **235**, 15-24.

Clarke A.G., Willison M.J. and Zeki E.M. (1984) A comparison of urban and rural aerosol composition using dichotomous samplers, *Atmos. Environ.*, **18**, 1767-1775.

Colvile R.N., Gómez-Perales J.E. and Nieuwenhuijsen M.J. (2003) Use of dispersion modelling to assess road-user exposure to $PM_{2.5}$ and its source apportionment, *Atmos. Environ.*, **37**, 2773-2782.

Dimashki M., Harrad S. and Harrison R.M. (2000) Measurements of nitro-PAH in the atmospheres of two cities, *Atmos. Environ.*, **34**, 2459-2469.

Dimashki M., Lim L.H., Harrison R.M. and Harrad S. (2001) Temporal trends, temperature dependence, and relative reactivity of atmospheric polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, **35**, 2264-2267.

Dockery D.W., Pope C.A., Xu X.P., Spengler J.D., Ware J.H., Fay M.E., Ferris B.G. and Speizer F.E. (1993), An association between air pollution and mortality in six U.S. cities, *New England Journal of Medicine*, 329, 1753-1759.

Donaldson K, Stone V, Gilmour P.S., Brown D.M. and MacNee W (2000) Ultrafine particles: mechanisms of lung injury, *Phil. Trans. R. Soc. Lond.* A, **358**, 2741-2749.

Dreher K.L., Jaskot R.H., Lehmann J,R., Richards J.H., McGee J.K., Ghio A.J. and Costa D.L. (1997) Soluble transition metals mediate residual oil fly ash induced acute lung injury, *J. Toxicol. Environ. Hlth.*, **50**, 285-305.

Dzubay T.G. and Barbour R.K. (1983) A method to improve the adhesion of particles on Teflon filters, *J. Air Pollut. Control Ass.*, **33**, 692.

Eatough D.J., Eatough N.L., Obeidi F., Pang Y.B., Modey W. and Long R. (2001) Continuous determination of $PM_{2.5}$ mass, including semi-volatile species, *Aerosol Sci. Technol.*, **34**, 1-8.

Eatough D.J., Obeidi F., Pang Y.B., Ding Y.M., Eatough N.L. and Wilson W.E. (1999) Integrated and real-time diffusion denuder sampler for $PM_{2.5}$, *Atmos. Environ.*, **33**, 2835-2844.

Fraser M.P., Buzcu B., Yue Z.W., McGaughey G.R., Desai N.R., Allen D.T., Seila R.L., Lonneman W.A. and Harley, R.A. (2003) Separation of fine particulate matter emitted from gasoline and diesel vehicles using chemical mass balancing techniques, *Environ. Sic. Technol.*, **37**, 3904-3909.

Ghio, A.J., Stonehuerner, J., Pritchard, R.J., Piantadosi, C.A., Quigley, D.R., Dreher, K.L. and Costa, D.L. (1996) Humic-like substances in air pollution particulates correlate with concentrations of transition metals and oxidant generation, *Inhal. Toxicol.*, **8**, 479-494.

Green D., Fuller G. and Barratt B. (2001) Evaluation of TEOM^{TM} 'correction factors' for assessing the EU Stage 1 limit values for PM_{10}, *Atmos. Environ.*, **35**, 2589-2593 (2001).

Harper S.L., Walling J.F., Holland D.M., Pranger L.J. (1983) Simplex pptimization of multielemental ultrasonic extraction of atmospheric particulates, *Analytical Chemistry*, **55**, 1553-1557.

Harrad S., Hassoun S., Callén Romero M.S. and Harrison R.M. (2003) Characterisation and source attribution of the semi-volatile organic content of atmospheric particles and associated vapour phase in Birmingham, UK, *Atmos. Environ*., **37**, 4985-499.

Harrison R.M. and Allen A.G. (1990) Measurements of atmospheric HNO_3, HCl and associated species on a small network in Eastern England, *Atmos. Environ*., **24**, 369-376.

Harrison R.M. and Jones M.R. (1995) The Chemical Composition of Airborne Particles in the UK Atmosphere, *Sci. Total Environ*., **168**, 195-214.

Harrison R.M., Msibi I.M., Kitto A.-M.N. and Yamulki S. (1994) Atmospheric chemical transformations of nitrogen compounds measured in the North Sea experiment, *Atmos. Environ*., **28**, 1593-1599.

Harrison R.M. and Yin J. (2000) Particulate matter in the atmosphere: Which particle properties are important for its effects on health?, *Sci. Tot. Environ*., **249**, 85-101.

Harrison R.M., Deacon A.R., Jones M.R. and Appleby R.S. (1997) Sources and processes affecting concentrations of PM_{10} and $PM_{2.5}$ particulate matter in Birmingham, UK., *Atmos. Environ.* **31**, 4103-4117.

Harrison R.M., Jones A.M. and Lawrence R.G. (2003b) A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites, *Atmos. Environ*., **37**, 4927-4933.

Harrison R.M., Jones M. and Collins G. (1999a) Measurements of the physical properties of particles in the urban atmosphere, *Atmos. Environ*., **33**, 309-321.

Harrison R.M., Shi J.P. and Jones M.R. (1999b) Continuous measurements of aerosol physical properties in the urban atmosphere, *Atmos. Environ*., **33**, 1037-1047.

Harrison R.M., Shi J.P., Xi S., Khan A., Mark D., Kinnersley R. and Yin J. (2000) Measurement of number, mass and size distribution of particles in the atmosphere, *Phil. Trans. R. Soc. Lond., A*, **358**, 2567-2580.

Harrison R.M., Smith D.J.T. and Luhana L. (1996) Source apportionment of atmospheric polycyclic Aromatic hydrocarbons collected from an urban location in Birmingham, UK, *Environ. Sci. Technol*., **30**, 825-832.

Harrison R.M., Smith D.J.T., Pio C.A. and Castro L.M. (1997) Comparative receptor modelling study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan), *Atmos. Environ.*, **31**, 3309-3321.

Harrison R.M., Smith D.J.T., Pio C.A., Castro L.M. (1997a) Comparative receptor modelling Study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). *Atmos. Environ.*, **31**, 3309-3321.

Harrison R.M., Tilling R., Callén Romero M.S., Harrad S. and Jarvis K. (2003a) A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment, *Atmos. Environ*., **37**, 2391-2402.

Harrison R.M., Yin J., Mark D., Stedman J., Appleby R.S., Booker J. and Moorcroft S. (2001) Studies of the coarse particle (2.5-10 μm) component in UK urban atmospheres, *Atmos. Environ.*, **35**, 3667-3679.

Heal M.R., Tunes T. and Beverland I.J. (2000) Using archive data to investigate trends in the sources and composition of urban PM_{10} particulate matter: Application to Edinburgh (UK) between 1992 and 1997, *Environ., Moni. Assess.*, **50**, 710-716.

Hjellbrekke A.-G., Schaug J., Hanssen J.E. and Skjelmoen J.E. (1997) Data report 1995, EMEP/CCC Report 4/97, Kjeller, Norway.

Ho K.F., Lee S.C., Chow J.C., Watson J.G. (2003) Characterization of PM_{10} and $PM_{2.5}$ source profiles for fugitive dust in Hong Kong, *Atmos Environ.*, **37**, 1023-1032.

Hoek G., Brunekreef B., Verhoeff A., Van Wijnen J. and Fischer P. (2000) Daily mortality and air pollution in the Netherlands, *J. Air Waste Mgt. Assoc.*, **50**, 1380-1389.

Hopke P.K., (1991) Receptor Modelling in Air Quality Management, Elsevier, Amsterdam.

Jones T., Blackmore P., Leach M., Berube K., Sexton K. and Richards R. (2002) Characterisation of airborne particles collected within and proximal to an opencast coalmine: South Wales, UK, *Environ, Moni. Assess.*, **75**, 293-312.

Jones T.P., Williamson B.J., BéruBé K.A. and Richards R.J. (2001) Microscopy and chemistry of particles collected on TEOM filters: Swansea, south Wales, 1998-1999, *Atmos. Environ.*, **35**, 3573-3583.

Kendall M., Hamilton R.S., Watt J. and Williams I.D. (2001) Characterisation of selected speciated organic compounds associated with particulate matter in London, *Atmos. Environ.*, **35**, 2483-2495.

Laden F., Neas L.M., Dockery D.W. and Schwartz J. (2000) Association of fine particulate matter from different sources with daily mortality in six U.S. cities, *Environmental Health Perspectives,* **108**, 941-947.

Lim L.H., Harrison R.M. and Harrad S. (1999) The contribution of traffic to atmospheric concentrations of polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, **33**, 3538-3542.

Lodge J.P.Jr. (1993) *Sampling Aerosols by filtration.* In: Methods of Air Sampling and Analysis. Lewis Publishers, Michigan, pp190-214.

Longley I.D., Gallagher M.W., Dorsey J.R., Flynn M., Allan J.D., Alfarra M.R. and Inglis D. (2003) A case study of aerosol (4.6 nm < D_p < 10 m) number and mass size distribution measurements in a busy street canyon in Manchester, UK, *Atmos. Environ.*, **37**, 1563-157.

Maenhaut W., Schwarz J., Cafmeyer J. and Chi X.G. (2002a) Aerosol chemical mass closure during the EUROTRAC-2 AEROSOL Intercomparison 2000, *Nuclear Instruments & Methods in Physics Research Section B-beam Interactions with Materials and Atoms*, **189**, 233-237.

Maenhaut W., Cafmeyer J., Dubtsov S. and Chi X.G. (2002b) Detailed mass size distributions of elements and species, and aerosol chemical mass closure during fall 1999 at Gent, Belgium, *Nuclear Instruments & Methods in Physics Research Section B-beam Interactions with Materials and Atoms*, **189**, 238-242.

Matthias-Maser S. and Jaenicke R. (1995) The size distribution of primary biological aerosol particles with radii >0.2 μm in an urban / rural influenced region, *Atmos. Res.*, **39**, 279-286.

Meyer M.B., Patashnick H., Ambs J.L. and Rupprecht E. (2000) Development of a sample equilibration system for the TEOM continuous PM monitor, *J. Air Waste Mgt. Assoc.*, **50**, 1345-1349.

Miguel A.G, Cass G.R., Glovsky M.M. and Weiss J. (1999) Allergens in paved road dust and airborne particles, *Environ. Sci. Technol.*, **33**, 4159-4168.

Moreno T., Gibbons W., Jones T. and Richards R. (2003) The geology of ambient aerosols: characterising urban and rural/coastal silicate $PM_{10-2.5}$ and $PM_{2.5}$ using high-volume cascade collection and scanning electron microscopy, *Atmos. Environ.*, **37**, 4265-4276.

Namdeo A.K., Colls J.J. and Baker C.J. (1999) Dispersion and re-suspension of fine and coarse particulates in an urban street canyon, *Sci. Total Environ.*, **235**, 3-13.

Oberdörster G. (2001) Pulmonary effects of inhaled ultrafine particles, *Int. Arch. Occ. Environ. Health*, **74**, 1-8.

Parsons B. and Salter L.F. (2003) Air quality effects of traffic in a canyon-like street (Falmouth, U.K.), *Environ., Moni. Assess.*, **82**, 63-73.

Pastor S.H., Allen J.O., Hughes L.S., Bhave P., Cass G.R. and Prather K. (2003) Ambient single particle analysis in Riverside, California by Aerosol Time-of-Flight Mass Spectrometry during the SCOS97-NARSTO, *Atmos. Environ.*, **37**(S2), S239-S258.

Peters A.J., Tomy G.T., Jones K.C., Coleman P. and Stern G.A. (2000) Occurrence of C_{10}-C_{13} polychlorinated n-alkanes in the atmosphere of the United Kingdom, *Atmos. Environ.*, **34**, 3085-3090.

Phillips N. (1997) Microscopical analysis of the role of fungal spores in suspended particulate matter in an urban garden scenario, BSc dissertation, University of Birmingham.

Pless-Mulloli T., King A., Howel D., Stone I. and Merefield J. (2000) PM_{10} levels in communities close to and away from opencast coal mining sites in Northeast England, *Atmos. Environ.*, **34**, 3091-3101.

Price M., Bulpitt S. and Meyer M.B., (2003) A comparison of PM_{10} monitors at a kerbside site in the northeast of England, *Atmos. Environ.*, **37**, 4425-4434.

Price M., O'Dowd C. and Dixon M. (2003) Interpretation of roadside PM_{10} monitoring data from sunderland, United Kingdom, *Environ., Moni. Assess.*, **82**, 225-241.

Qin Y. and Oduyemi K. (2003a) Chemical composition of atmospheric aerosol in Dundee, UK, *Atmos. Environ.*, **37**, 93-104.

Qin Y. and Oduyemi K. (2003b) Atmospheric aerosol source identification and estimates of source contributions to air pollution in Dundee, UK, *Atmos. Environ.*, **37**, 1799-1809.

QUARG (1996) Third Report of the Quality of Urban Air Review Group, *Airborne Particulate Matter in the UK*, Department of the Environment, London.

Salma I., Maenhaut W., Zemplén-Papp É., Záray G. (2001) Comprehensive characterisation of atmospheric aerosols in Budapest, Hungary: Physicochemical properties of inorganic species, *Atmos. Environ.*, **35**, 4367-4378.

Salter L.F. and Parsons B. (1999) Field trials of the TEOM and Partisol for PM_{10} monitoring in the St Austell china clay area, Cornwall, UK, *Atmos. Environ.*, **33**, 2111-2114.

Schaap M., Müller K. and ten Brink H.M. (2002) Constructing the European aerosol nitrate concentration field from quality analysed data, *Atmos. Environ.*, **36**, 1323-1335.

Schauer J.J., Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. and Simoneit B.R.T. (1996) Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, **30**, 3837-3855.

Schwartz J., Dockery D.W. and Neas L.M. (1996) Is Daily Mortality Associated Specifically with Fine particles?, *J. Air Waste Manage. Assoc.*, **46**, 927-939.

Shi J.P., Evans D.E., Khan A.A., and Harrison R.M. (2001) Sources and concentration of nanoparticles (< 10 nm diameter) in the urban atmosphere, *Atmos. Environ.*, **35**, 1193-1202.

Shi J.P., Khan A.A. and Harrison R.M. (1999a) Measurements of ultrafine particle concentration and size distribution in the urban atmosphere, *Sci. Total Environ.*, **235**, 51-64.

Soutar A., Watt M., Cherrie J.W. Seaton A. (1999) Comparison between a personal PM_{10} sampling head and the tapered element oscillating microbalance (TEOM) system, *Atmos. Environ.*, **33,** 4373-4377.

Stedman J.R., Linehan E. and Conlan B. (2001) Receptor modelling of PM_{10} concentrations at a United Kingdom national network monitoring site in central London, *Atmos. Environ.*, **35**, 297-304.

Stedman J.R. (1997) The secondary particle contribution to elevated PM_{10} concentrations in the UK, AEA Technology, National Environmental Technology Centre, Report 20008001/007.

Stedman J.R. (2002) The use of receptor modelling and emission inventory data to xxplain the downward trend in UK PM_{10} concentrations, *Atmos. Environ.*, **36**, 4089-4101.

Thurston G.D. (1983) A source apportionment of particulate air pollution in metropolitan Boston, Doctoral dissertation, Dept. of Environ. Health Sci., School of Public Health, Harvard University, Boston, Massachusetts.

Thurston G.D., Spengler J.D. (1985) A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston, *Atmos. Environ.*, **19**, 9-25.

Ward D.J., Roberts K.T., Jones N., Harrison R.M., Ayres J.G., Hussain (2002) Normal and asthmatic children, *Thorax*, **57**, 489-502.

Wichmann H.E. and Peters A. (2000) Epidemiological evidence of the effects of ultrafine particle exposure, *Phil. Trans. R. Soc. Lond. A*, **358**, 2751-2769.

Yin J. (2002) Monitoring airborne particulate mass and number concentrations in the UK atmosphere, PhD thesis, the University of Birmingham.