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SOURCES AND PROPERTIES OF AIRBORNE PARTICULATE MATTER

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1. EXECUTIVE SUMMARY

(1) The main purpose of the work described in this report is to evaluate the newly developing technique of Single Particle Mass Spectrometry to understanding the chemistry, sources and atmospheric transformations of airborne particulate matter relevant to human health. Commercial instruments for single particle mass spectrometry have only recently come available and this is therefore the first such appraisal, although work is in hand in other countries (e.g. by the USEPA).

(2) The advantage offered by Single Particle Mass Spectrometers relative to pre-existing means of characterising airborne particles is that the Single Particle Mass Spectrometer (SPMS) is able to generate information individually on the chemical composition of large numbers of particles as a function of their size rather than integrating that information across all of the particles collected over a period of hours, as happens with traditional bulk chemical measurements. It therefore provides direct information on the chemical associations of different elements within individual particles, whilst traditional bulk analysis would require uncertain inferences to be drawn regarding such chemical associations.

(3) Although not anticipated in the original proposal, this work has had the considerable advantage of access to two SPMS instruments, the German LAMPAS (Laser Mass Analysis of Particles in the Airborne State) and the American ATOFMS (Aerosol Time-of-Flight Mass Spectrometer). The two instruments have a great deal in common, but have slightly different operational principles and capabilities and different desorption/ionisation lasers. Whilst the ATOFMS was operated with an Nd:Yag 266 nm laser, the LAMPAS was operated both with a nitrogen laser (337 nm) and an
excimer laser (193 nm). During some of the fieldwork it was possible to compare the performance of the two instruments in the field.

(4) The SPMS instruments operate by drawing in ambient air and creating a beam of individual particles from which the supporting gases are pumped away. The individual particles are sized according to their velocities as they accelerate into the vacuum of the instrument and are then vaporised and ionised by firing a powerful laser (the desorption/ionisation laser). The energy of the desorption/ionisation process is sufficient to break the particle into atomic and simple ionic fragments, which, because they are charged, can be identified by measurement of simultaneous negative and positive ion mass spectra using two time-of-flight mass spectrometers. Thus, chemical composition information is generated on individual particles and the instrument is able to analyse in excess of 10 particles per minute, thus generating very large sets of data.

(5) Experiments in the laboratory with simple chemical compounds have given insights into interpretation of the mass spectra. Metals are generally identifiable from single charged positive ions whilst anions such as chloride, nitrate and sulphate yield simple and easily recognised fragments in the negative ion spectrum. Carbonaceous materials tend to give regular patterns in both the positive and negative ion spectra with differences readily identifiable between elemental (black) carbon and organic compounds.

(6) In addition to mass spectral interpretation from simple ion fragments of particles, work has also been conducted in the laboratory to characterise the mass spectra derived from model environmental materials contributing to the load of airborne particles. These include diesel engine exhaust, petrol engine exhaust, road dust, soil, plant fragments, tyre dust and brake dust. The characteristic mass spectral fingerprints generated by
these materials can then be compared with mass spectral data obtained from individual airborne particles providing a means of source apportionment.

(7) The SPMS instruments have been deployed in a number of field campaigns in which complementary data such as bulk chemical analysis of particulate matter, particle size distributions and gas phase pollutant concentrations have also been determined. The main campaigns have been carried out in Birmingham (Winter and Summer campaigns in conjunction with the NERC-funded PUMA project), London (Summer and Winter campaigns at roadside and background locations), and Birmingham involving an intercomparison of data collected in a road tunnel at roadside and at a nearby urban background location. The measurement campaigns have used respectively the LAMPAS alone, the LAMPAS and ATOFMS, and the ATOFMS instrument alone. Work in both Birmingham and London with the LAMPAS has used the Ford Mobile Laboratory with a large range of complementary measurement instruments.

(8) Qualitative appraisal of mass spectral instrumentation emphasises the very different sensitivities of the SPMS instruments to different ion fragments. Thus, the LAMPAS (especially) is of exceptionally high sensitivity to potassium and sodium whilst giving a very poor response to ammonium. These differential sensitivities provide a very real difficulty in quantitative spectral interpretation. Inter-ion sensitivity differentials are generally lower with the ATOFMS than for the LAMPAS.

(9) Measurements made during the PUMA campaigns in Birmingham have used the LAMPAS, employing four of its fixed particle sizes at 0.5 µm, 1.0 µm, 1.5 µm and 2.0 µm. A range of polluted and relatively unpolluted airmasses were encountered and the mass spectra have been interpreted both as hourly averages of the collected spectral data
and from individual mass spectra. Marked changes in particle composition can be recognised from the mass spectral patterns as the airmasses change.

(10) The LAMPAS instrument has an associated fuzzy clustering software, which although laborious to use, categorises particles according to their mass spectral patterns in a broadly useful manner. Application of the fuzzy clustering software during the Winter PUMA campaign allowed a number of particle classes to be recognised, termed elemental carbon, aged carbon (two different patterns), carbonaceous inorganic salt, mineral and inorganic, nitrogen-rich and sulphur-rich. These provide a potential basis for distinguishing between primary carbonaceous particles from combustion sources, mineral materials from resuspended soil and road dust and sulphates and nitrates from long-range transport of regional aerosol. Comparison of data from south-westerly and northerly wind sectors using the fuzzy clustering method gave realistic changes in the particle make-up in relation to the seven identified classes of particle.

(11) Examination of particle spectra during a pollution episode in the Summer PUMA campaign based on the presence or absence of certain characteristic spectral peaks allowed classification into the following particle types: nitrate only, sulphate only, elemental carbon, secondary, mixed nitrate plus sulphate, sodium/potassium, aged carbon and others. Compared to bulk chemical analysis, the results generated in this way over-emphasise the importance especially of sodium and potassium-containing particles.

(12) The application of fuzzy clustering to characterising particles in the Winter PUMA campaign gave the following particle types: elemental carbon, aged carbon, carbonaceous inorganic, nitrate-rich, sulphate-rich, mixed inorganic salt, sodium-rich
salt and potassium rich salt. Again, the clustering process greatly over-emphasises the abundance of potassium (particularly) and sodium-rich particles whilst the relative abundances of other species look realistic in relation to bulk chemical data.

(13) Two measurement campaigns were conducted during 2001 in central London. In each campaign, measurements were located at two sites, one at roadside, one urban background. In the Winter campaign, SPMS data were collected with the LAMPAS; during the Summer campaign both the LAMPAS and ATOFMS instruments were used. In both campaigns, a large range of complementary data were collected.

(14) Both polluted continental air and relatively clean air of maritime origins were sampled during these campaigns giving a strong compositional contrast against which to judge the SPMS instruments. Measured particle size distributions using a Scanning Mobility Particle Sizer and Aerodynamic Particle Sizer were fairly typical during the sampling periods. Elemental and organic carbon measurements correlated with NOx suggesting local road traffic as the major contributor to these species.

(15) Interpretation of differences between the roadside and urban background site were complicated by the fact that the two sites were not sampled simultaneously. One noticeable difference, however, was in the trace metal peaks determined at the roadside location indicative of contributions of road dust and brake dust to airborne particle loadings. The roadside site also showed a far greater abundance of particles in the aged carbon category than measured at the background site.

(16) Bulk chemical data collected during the London Summer campaign showed the anticipated difference between roadside and urban background site especially in relation
to elemental and organic carbon concentrations and the correlation of carbon with NO$_x$. LAMPAS count rates reached 50 per minute as a result of use of the new excimer laser. This produced ion fragments which had not been seen before which appeared to be related to breakdown of hydrocarbon materials.

(17) Extensive efforts were made to generate a quantitative comparison between the abundance of species as measured by the LAMPAS and ATOFMS, and bulk chemical data collected either using a dichotomous Partisol sampler (PM$_{2.5}$ and coarse particles) or narrower size fractions collected using a MOUDI cascade impactor. Such attempts initially used the occurrence of mass spectral peaks characteristic of specific ions and made corrections for particle size, inlet efficiency of the SPMS instrument and instrumental relative sensitivities. For certain of the species, particularly potassium and nitrate, it was possible to achieve very good correlations between the relative concentrations measured with the LAMPAS and concentrations measured with the Partisol instrument. For other components of the particles, the correlations were less strong, possibly indicative of spectral interferences. Attempts were made with the ATOFMS data to reconstruct composition information derived from bulk analysis of Partisol and MOUDI samples and using relative sensitivity factors derived from field measurements. Whilst the latter brought about an improvement in the relative abundance estimates these were still far from good.

(18) A campaign was conducted in Birmingham during 2002 involving use of the ATOFMS instrument at three sites: the Queensway Tunnel in central Birmingham, the Bristol Road, a major A-road running through suburban Birmingham, and Winterbourne, a nearby urban background site. The ATOFMS is capable of measuring different particles sizes without adjustment, unlike the LAMPAS which has to be set for a given particle
size. Therefore, data have been analysed according both to dependence on particle size, as well as the location of sampling.

(19) The measurements of the Queensway Road Tunnel give an excellent source profile for road traffic emissions. These are clearly dominated in the smaller size fractions by exhaust emission from diesel vehicles, whilst moving to coarser particle sizes, particles arising from road dust, tyre wear and brake dust progressively become dominant within the mass spectral patterns.

(20) Data from the Bristol Road site show an important influence of the road traffic signature seen in the Queensway Tunnel site. This is, however, modified by a greater influence of sulphate and nitrate particles, presumably deriving from regional transport. Particles containing polycyclic aromatic hydrocarbons are also very evident at this location. The coarse particle size ranges at this site show a strong influence of sodium chloride, presumably arising from sea salt.

(21) At the Winterbourne background site, very few particles were observed in the smallest measurable size fractions (e.g. 0.2-0.3 μm diameter). The coarser particles at this site show strong evidence of sodium chloride presence, with peaks characteristic of nitrates, sulphates and carbon also readily observable.

(22) Extensive laboratory work has been conducted to characterise the mass spectra of typical urban particulate source materials including diesel exhaust, petrol exhaust, soil, road dust, brake dust, tyre fragments and leaf/plant debris. The results emphasise the complexity of, for example, particles derived from the brake linings of different vehicles. A considerable range of spectra can be obtained even from a single brake shoe
indicating a rather heterogeneous composition to the brake shoe with particle fragments having a range of compositions. Certain components, however, such as barium are strongly characteristic of brake dust particles.

(23) Selection criteria have been derived based upon the presence or an absence of particular mass spectral peaks which allow the allocation of measured particles into the various particle source categories. These have been applied to air samples collected at the Queensway Road Tunnel and Bristol Road sites in Birmingham. The spectral fingerprints generated in the laboratory studies are clearly recognisable in the airborne particles, although at the present stage of development, the technique probably does not allow accurate quantification of the contribution of such particle types to airborne particle mass.

CONCLUSIONS

(24) The single particle mass spectrometry technique is an extremely powerful way of characterising the chemical composition of individual airborne particles.

(25) The results of examining mass spectra of individual airborne particles emphasise the complexity of composition of many particles which can result from atmospheric processes such as coagulation and condensation of vapours. However, some particles of very simple composition are also readily identifiable.

(26) The SPMS instruments show differential sensitivities to different chemical components of particles and this tends to lead to an over-emphasis upon species for which the instrument has very high sensitivity (especially potassium and sodium). This problem needs to be addressed in data interpretation.
(27) Use of the fuzzy clustering software of the LAMPAS SPMS instrument provides an interesting but as yet not wholly realistic characterisation of the different kinds of particle in the atmosphere. It gives far too much emphasis to particles containing those elements to which the instrument is especially sensitive.

(28) Reconstruction of particle bulk composition based upon the presence of indicator peaks in the mass spectra shows promise but does not at present give a quantitative comparison to the results of bulk chemical procedures. This may be the result of spectral overlaps for some chemical species, which would need to be investigated further. Should this problem be resolved, the instruments would be a powerful means of generating information on the chemical composition of airborne particulate matter with much higher temporal resolution than is typically available at present.

(29) Measurements at sites with different degrees of traffic influence in Birmingham have shown very major compositional differences in airborne particles and a ready recognition of traffic-generated particles both from engine exhaust and non-exhaust sources. There is a very clear transition in particle composition on going from fine particles, which are dominated by diesel engine exhaust, to coarse particles where road dust and vehicle wear components become dominant.

(30) Fingerprinting techniques based on recognition of the composition of model particles generated in the laboratory need further development but offer a tremendous potential for characterising and quantifying the contribution of sources such as brake wear, tyre wear and road dust resuspension to airborne particle number and mass.
(31) Extension of the current size range of the SPMS instruments (approximately 0.2 µm to 3 µm) would be highly beneficial in terms of characterisation and source apportionment of the finest and coarsest particles within the PM$_{10}$ size range.
2. **PREAMBLE: THE CONTRACT**

The outcome of this research is used to inform policy at DEFRA and the devolved administrations. The devolved administrations are as follows: the National Assembly for Wales (NAW), the Northern Ireland Executive, represented by the Department of the Environment in Northern Ireland (DoENI), and the Scottish Executive, represented by the Scottish Executive Environment and Rural Affairs Department (SEERAD).

This contract was established in January 2000 between the Department of the Environment, Transport and the Regions (now the Department for Environment, Food and Rural Affairs) and the University of Birmingham. The main purpose of the contract was to investigate the applicability of single particle mass spectrometry as a technique for real-time characterisation of airborne particulate matter and to exploit the availability of a prototype instrument owned by the Ford Motor Company at a time when commercial instruments were at that stage unavailable.

By operating the single particle mass spectrometry instrumentation alongside other instruments for measuring concentrations of atmospheric gases and particles, it was hoped to achieve the following outcomes:

(a) A more complete spatial and temporal characterisation of the particle size distribution of PM$_{10}$ than is currently available, for a range of locations.

(b) Size-discriminated chemistry of airborne particulate matter in the UK atmosphere at a range of locations.

(c) A understanding of the influence of locality and local sources upon airborne particle composition, through improved source apportionment and temporal resolution.
(d) Information on the spatial and temporal evolution of particle size distributions in the urban atmosphere.

(e) An intercomparison of state-of-the-art measurement techniques for airborne particulate matter.
3. AIRBORNE PARTICULATE MATTER AND SINGLE PARTICLE MASS SPECTROMETRY

3.1 INTRODUCTION

In recent years there has been a growing concern about the adverse impacts which particulate matter may have on health. Many epidemiological studies have indicated that there is a strong link between increases in particulate matter finer than 10 µm (PM$_{10}$) and increased mortality and morbidity from all causes (Dockery et al., 1993). This has led to the adoption of air quality standards, and in Europe, the limit values to be achieved by 2005 are a 50 µg m$^{-3}$ 24-hour mean not to be exceeded more than 35 times per year and an annual mean of 40 µg m$^{-3}$.

3.2 SOURCES AND SIZE DISTRIBUTION

Traditionally, atmospheric particles have been divided into three size classes:

- **Nucleation mode** – Consists of particles generally less than 0.1 µm usually formed by gas-to-particle conversion processes or by direct emission.

- **Accumulation mode** – Consists of particles between 0.1 - 1 µm that represents a region of particle growth due to condensation and coagulation.

- **Coarse mode** – Consists of particles greater than 1 µm reflecting the major formation mechanism; mechanical abrasion processes, such as wind-driven resuspension. For historical reasons the instrumental division between coarse and fine particles is normally represented by a cut at 2.5 µm, but this leads to some incorporation of coarse mode particles in the fine fraction.

Figure 3.1 illustrates a common urban aerosol distribution presented in number, surface, and volume. It shows that if number of particles is considered, then the bulk of particles exist in the nucleation mode, whereas if surface area is the metric, this lies predominantly in the accumulation mode.
Figure 3.1. A common urban aerosol distribution presented in number, surface area, and volume distributions.

Airborne particulate matter originates from both biogenic and anthropogenic sources, which are extremely diverse adding to the difficulty of source apportionment. There is a wide range of biological particles in the atmosphere in the form of bacteria, fungal spores and pollens. They have a considerable size range for example, pollen grains

Source: based on Whitby (1978).
can have diameters greater than 10 µm, whilst most bacteria have diameters around 1 µm and viruses are even smaller than this (APEG, 1999). Many particles such as pollens and fungal spores enter the atmosphere preformed, whilst others are produced ‘in situ’ by the chemical reactions of gases and the condensation of vapours. Figure 3.2 illustrates the processes involved in the formation and evolution of aerosol particles.

Figure 3.2. Schematic diagram of the large range of sizes and that are involved in the formation and evolution of aerosol particles, and how aerosols participate in atmospheric chemical processes through homogeneous, heterogeneous and in-cloud reactions (F. Raes et al., 2000).

Secondary aerosol sources can be attributed to natural and man-influenced processes. Research has shown that aerosols are formed if various volatile organic compounds (VOCs) are mixed with air and nitrogen oxide (NO₂) and irradiated resulting in the formation of photochemical smog (Cadle et al., 1972). This phenomenon has been observed in remote (Blue Mountains, New South Wales, Australia) and urban environments, due to the presence of VOCs emitted from plants and vehicles respectively. NO₂ also occurs naturally due to the formation (sources include forest fires and electrical storms) and transformation of nitrogen oxide (NO). Other natural sources of particulates include the emission of mineral dust by
wind erosion and the production of sea-salt particles at the ocean surface. It is recognised that mineral dust plays an important role in the tropospheric chemistry due to heterogeneous interactions with nitrogen and sulfur compounds (Dentener et al., 1996).

Anthropogenic sources of primary particulate matter have been well studied. Current inventories have mainly measured particles in the PM$_{10}$ size range, without further size fractionation, however, recent data has been collected below 2.5 $\mu$m, 1.0 $\mu$m and 0.1 $\mu$m allowing inventories for UK emissions of PM$_{2.5}$, PM$_{1}$ and PM$_{0.1}$ to be estimated. The main primary sources of PM$_{10}$ in the UK are:

- **Road Transport** – Traffic generated particulate emissions have many sources. Not only are there contributions from the tail pipes of vehicles, but also particles produced mechanically by the wearing of tyres, clutch linings, brake linings and road surfaces. These particles can be deposited on to the road surface along with soil and plant materials, which are pulverized and resuspended by oncoming traffic. It is known that a significant amount of coarse particulate material above urban background levels is derived from resuspension of road surface dusts. The resuspension of road dust is not presently included in emission inventories as further measurements are required to quantify the individual sources that contribute to road dust.

- **Stationary sources** – Emissions from stationary sources have been declining for various reasons. Domestic coal burning used to be a major contributor to particulate emissions though in 1996 national emissions had reduced to 14 % (APEG, 1999).

- **Industrial and agricultural sources** – A range of industrial processes lead to the release of dust, including activities such as mining and quarrying. Agriculture is also a source of particulate matter emissions, as yet poorly quantified.
3.3 ATMOSPHERIC AEROSOL COMPOSITION

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

Formation and transformation of atmospheric particles

Many aerosols enter the atmosphere preformed, for example soil particles dispersed by the wind. Others are produced ‘in situ’ by chemical reactions of gases and condensation of vapours. Whatever their mode of introduction into the atmosphere most particles undergo chemical transformations in the atmosphere which depend on their initial compositions, their atmospheric residence times, and the surrounding air composition. Commonly occurring crystalline components of aerosols to be found in the troposphere are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Aerosol species</th>
<th>Chemical formula</th>
<th>Relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>Major</td>
</tr>
<tr>
<td>Ammonium hydrogen sulfate</td>
<td>NH₄HSO₄</td>
<td>Major</td>
</tr>
<tr>
<td>Letovicite</td>
<td>(NH₄)₂SO₄, NH₄HSO₄</td>
<td>Major</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>Major</td>
</tr>
<tr>
<td>Metal ammonium sulfates</td>
<td>(NH₄)₂SO₄,MSO₄ (M = metal)</td>
<td>Minor</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>NH₄NO₃</td>
<td>Major</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>NaNO₃</td>
<td>Minor</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH₄Cl</td>
<td>Minor</td>
</tr>
</tbody>
</table>

Table 3.1. Major secondary aerosol components
(Harrison and Van Grieken, 1998).
Sulfates

Sulfates comprise a major proportion of aerosols in the troposphere and the stratosphere. Some sulfur containing gases originate from the oceans (i.e. dimethylsulfide (DMS)), other natural sources include volcanic activity releasing sulfur dioxide (SO\(_2\)) and the decay of organic matter in the biosphere producing hydrogen sulfide (H\(_2\)S), DMS, and dimethyldisulfide ((CH\(_3\))\(_2\)S\(_2\)). These compounds can be oxidised by the attack of hydroxyl (OH) and nitrate radicals (NO\(_3\)). Homogeneous gas phase reactions of SO\(_2\) to produce sulphate are known as well as heterogeneous processes that can occur in cloud, fog, or aerosol droplets. The most significant reaction is the oxidation of SO\(_2\) with OH (Stockwell et al, 1983)

\[
\begin{align*}
SO_2 + OH + M &\rightarrow HSO_3 + M \\
HSO_3 + O_2 &\rightarrow SO_3 + HO_2 \\
SO_3 + H_2O &\rightarrow H_2SO_4
\end{align*}
\]

Where M = N\(_2\) or O\(_2\). The H\(_2\)SO\(_4\) vapour formed nucleates to form sulphuric acid droplets, and can grow by condensing water vapour. The initial nuclei formed can grow by coalescing with each other by Brownian aggregation and by coagulation with other pre-existing particles. These processes lead to a distribution of sizes ranging from 10 nm to 1 \(\mu\)m. The rate of the nucleation and accumulation are rapid compared to the rate of oxidation of SO\(_2\) therefore, the formation of H\(_2\)SO\(_4\) is dependent on the concentration of OH, which is formed predominantly during the daytime. Due to the mechanism being driven by sunlight the process also occurs to a greater extent during the summer. During the winter months other routes to the oxidation of SO\(_2\) in the presence of cloud droplets are predominant. As this route involves pre-existing droplets it does not lead to an increase in particle number, but leads to an increase in particle mass. In the presence of liquid water the following equilibria are established:

\[
SO_2 \ (g) + H_2O \rightleftharpoons SO_2.H_2O
\]
SO$_2$H$_2$O $\rightleftharpoons$ HSO$_3^-$ + H$^+$

HSO$_3^-$ $\rightleftharpoons$ SO$_3^{2-}$ + H$^+$

Photochemical and cloud oxidation of SO$_2$ occur on very similar timescales and spatial scales (30 – 50 hours and 500 – 300 km), though usually with varying seasonal intensities and in different air masses (APEG, 1999).

The acidic aerosols formed can also carry on to form ammonium sulfate by taking up NH$_3$, through the reactions:

\[
\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4
\]

\[
\text{NH}_3 + \text{NH}_4\text{HSO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4
\]

The main sources of NH$_3$ are agricultural in origin, for example through the use of fertilisers and the disposal of animal waste to land, although emissions from road vehicles are becoming more important.

**Nitrates**

There is little primary particulate nitrate matter in the atmosphere. In general nitrate occurs in the atmosphere due to the formation of nitric acid (major pathways shown below), which can then form particles by reacting with ammonia or sodium chloride.

Formation of nitric acid during the day:

\[
\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3
\]

Where the major formation of OH during the day is due to the initial photolysis of O$_3$. At night-time the rate of production of OH drops and other mechanisms take over:

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2
\]

This process will only occur at night as the nitrate radical is readily photolysed during the day. NO$_3$ can carry on to form nitric acid by the pathways:

\[
\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5
\]

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3
\]
And, 

\[ \text{NO}_3 + \text{RH} \rightleftharpoons \text{HNO}_3 + \text{R} \]

Although nitric acid, ammonium nitrate and nitrogen pentoxide all have relatively low volatilities compared with NO\textsubscript{x} they are unable to undergo homogeneous nucleation. Instead, they attach themselves to pre-existing particles to undergo heterogeneous nucleation. The conversion of HNO\textsubscript{3} to particulate matter can occur through the reaction with ammonia and sodium chloride. In the marine atmosphere the concentration of ammonia is low so the major pathway is via:

\[ \text{HNO}_3 (g) + \text{NaCl} (a) \rightarrow \text{NaNO}_3 (a) + \text{HCl} (g) \]

Or via nitrogen pentoxide,

\[ \text{N}_2\text{O}_5 (g) + \text{NaCl} (a) \rightarrow 2\text{NaNO}_3 (a) + 2\text{HCl} (g) \]

Evidence for this sea-salt displacement mechanism has been seen using aerosol time-of-flight mass spectrometry (ATOFMS) as shown in Figure 3.3. (Gard et al., 1998).

Figure 3.3. The chloride replacement reaction observed at Long Beach, CA, 1996 (Gard et al., 1998).
Chlorides

The main source of particulate chloride is marine aerosol. Contributions are also possible from road salt, but this is very poorly quantified, and ammonium chloride, although formation of the latter semi-volatile compound in the UK air is now unfavourable due to low concentrations of its precursor, hydrogen chloride.

3.4 THE DEVELOPMENT OF ON-LINE ANALYTICAL TECHNIQUES FOR ATMOSPHERIC PARTICLES

Unfortunately, the traditional methods of collection followed by off-line analysis have many disadvantages including:

- The volatilisation of semi-volatile compounds during sampling is known to occur for species like ammonium nitrate and semi-volatile organics.
- The particles may undergo chemical and physical transformation during transport and storage (Chow, 1995).
- Sampling is usually required over lengthy periods (hours to days).
- Sampling methods involve collecting size-segregated bulk samples, which provide data representing an average chemical composition of the particles. No information on the composition of individual particles can be derived.

These disadvantages create difficulties in characterizing the aerosol and apportioning the source. The development of instruments for on-line data collection and real-time measurements has offered considerable advantages. The time resolution of the data has improved greatly, along with a reduction in the time required between sampling and analysis.

The most significant advance in aerosol measurements has been through the development of on-line analysis with mass spectrometry (MS). Table 3.3 gives a historical summary of the major achievements that have been made to date in this research area.
Table 3.3. Development of on-line particle mass spectrometry.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sizing Method</th>
<th>Ionization Method</th>
<th>Mass Spectrometer</th>
<th>Achievements</th>
</tr>
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<tbody>
<tr>
<td>Davis, 1973</td>
<td>Ion signal intensity</td>
<td>Surface/thermal</td>
<td>Single focusing</td>
<td>Began the field of on-line single particle MS</td>
</tr>
<tr>
<td></td>
<td>None</td>
<td>Magnetic sector</td>
<td>Quadrupole</td>
<td>Introduced quadrupole to SPMS</td>
</tr>
<tr>
<td>Lassiter and Moen, 1974</td>
<td>None</td>
<td>Surface/thermal</td>
<td>Quadrupole</td>
<td>Introduced Ru oven allowing lower particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>detection limits</td>
</tr>
<tr>
<td>Myers and Fite, 1975</td>
<td>Ion signal intensity</td>
<td>Surface/thermal</td>
<td>Quadrupole</td>
<td>Combined surface ionisation and EI</td>
</tr>
<tr>
<td></td>
<td>Aerodynamic sizing (monodisperse)</td>
<td>LDI</td>
<td>Quadrupole//magnetic sector</td>
<td>Introduced LDI to SPMS</td>
</tr>
<tr>
<td>Allen and Gould, 1981</td>
<td>Ion signal intensity</td>
<td>Surface/thermal</td>
<td>Quadrupole</td>
<td></td>
</tr>
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<td>Sinha et al, 1984,</td>
<td>Aerodynamic sizing (polydisperse)</td>
<td>LDI</td>
<td></td>
<td></td>
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<td>McKeown et al., 1991</td>
<td>LDI</td>
<td>Reflectron TOF</td>
<td></td>
<td>Constructed first on-line TOFMS</td>
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<td>Prather et al, 1994</td>
<td>Aerodynamic sizing (polydisperse)</td>
<td>LDI</td>
<td>Reflectron TOF</td>
<td>Applied precise sizing technique</td>
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<tr>
<td>Hinz et al., 1994</td>
<td>LDI</td>
<td>Reflectron TOF</td>
<td></td>
<td>First to use and report + and – spectra for a single</td>
</tr>
<tr>
<td></td>
<td>LDI</td>
<td>Reflectron TOF</td>
<td></td>
<td>particle</td>
</tr>
<tr>
<td>Murphy, 1995</td>
<td>Light-scattering intensity</td>
<td>Reflectron TOF</td>
<td></td>
<td>Employed SPMS in stratospheric measurements</td>
</tr>
<tr>
<td>Reents et al., 1995</td>
<td>None</td>
<td>Reflectron TOF</td>
<td></td>
<td>First to analyse ultrafines as small as 20 nm.</td>
</tr>
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<td></td>
<td></td>
<td>Reflectron TOF</td>
<td></td>
<td>Technique suffers from a low ablation rate.</td>
</tr>
<tr>
<td>Ge et al., 1998</td>
<td>Size selective inlet</td>
<td>Reflectron TOF</td>
<td></td>
<td>Developed an inlet capable of focusing the</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reflectron TOF</td>
<td></td>
<td>particle beam, improving ablation rate.</td>
</tr>
<tr>
<td>Galli et al., 2001</td>
<td>SMPS</td>
<td>Reflectron TOF</td>
<td></td>
<td>Used an SMPS to improved particle detection down to 8 nm.</td>
</tr>
</tbody>
</table>

3.5 **LASER MASS ANALYSIS OF PARTICLES IN THE AIRBORNE STATE (LAMPAS)**

Hinz et al. (1994) developed an instrument by the name of Laser Mass Analysis of Particles in the Airborne State (LAMPAS). The LAMPAS is a transportable system, designed for physical and chemical analysis of aerosols. The instrument works on the principle of laser desorption ionisation (LDI) mass spectroscopy. It utilizes a single HeNe laser with two photomultiplier tubes (PMTs) for particle detection, a nitrogen laser for deposition/ionisation (DI) and a time-of-flight mass spectrometer (TOFMS) with multichannel plates (MCP) for ion detection.
The aerosol particles enter the system at atmospheric pressure via a differentially pumped inlet. The inlet system consists of three consecutive stages that allows for efficient particle transfer into the mass spectrometer whilst pumping away the carrier gas. The particles pass an orifice into the TOF chamber that is maintained at a pressure of approximately $10^{-6}$ hPa by a turbo molecular pump. The path the particles take is shown in Figure 3.4. On entering the TOF chamber the particles cross the path of the HeNe laser causing light to be scattered and detected by two PMT producing two PMT signals, which are processed by a coincidence unit. A signal from both PMTs is required for an output signal to be generated. The output pulse is used to trigger the DI laser. A delay time between the detection laser and the DI laser can be set and varied allowing different particle sizes to be analysed. As shown in Figure 3.4 two separate microchannel plates detect both positive and negative ions with a drift tube ensuring a field-free flight of negative ions. The detection efficiency (ratio of the number of particles introduced into the system to the number of analysed particles) is between $10^{-5}$ for particles with 200 nm diameter and $10^{-3}$ for particles with 800 nm diameter.
3.6 AEROSOL TIME-OF-FLIGHT MASS SPECTROMETRY (ATOFMS)

The ATOFMS is the first commercially available single particle mass spectrometer. Figure 3.5 illustrates the experimental set up of the ATOFMS. Particles are sampled from the atmosphere through a nozzle and two differentially pumped skimmers, removing the excess gas molecules whilst collimating the particles into a narrow beam. The particles are detected and aerodynamically sized by two orthogonal continuous-wave argon lasers. The time taken for a particle to move between the lasers is monitored by a logic circuit, which controls the desorption/ionisation laser Nd:YAG laser (266 nm). Therefore, firing the laser when the particle enters the centre source region. The positive and negative ions produced are separated by a time-of-flight mass spectrometer (TOFMS) with ions of different mass to charge ratios (m/z) reaching the detector at different times.

![Figure 3.5. Schematic diagram of ATOFMS](image-url)
4. PUMA CAMPAIGNS

4.1 INTRODUCTION

Two PUMA campaigns (Summer 1999 and Winter 1999/2000) took place as part of the Natural Environment Research Council – funded project entitled “Pollution of the Urban Midlands Atmosphere” (PUMA).

4.2 DATA COLLECTION

The majority of the data collected by the LAMPAS during both the Summer and Winter PUMA sampling campaigns were acquired during intensive monitoring periods when atmospheric conditions reflected air masses that could be classified as either clean or polluted. The majority of air masses arriving in Birmingham tended to come from the west after travelling across the Atlantic Ocean. If these air masses did not cross areas of industrialisation or high population, for example by traversing the less industrial region of the south-west, then the air mass could be classified as clean. On a number of occasions the air mass arriving in Birmingham had approached from a more easterly direction after crossing the industrial areas of northern Germany or the highly populated areas lying south-east of Birmingham. Under these circumstances more polluted air masses were encountered, and the LAMPAS, together with bulk particle methods were run intensively.

4.3 DATA ANALYSIS

The data collected by the LAMPAS has been processed in such a way as to use hourly average mass spectra to probe the data initially for any significant changes in composition. If any changes were observed, the individual spectra were then referred to. Corresponding bulk chemical analysis data were also used so that spectra occurring during episodes of great disparity can be compared and again the single spectra can be inspected. An automated
classification process, known as Fuzzy Clustering, that has been specifically developed for classifying spectra generated by the LAMPAS was also employed.

4.4 SUMMER PUMA CAMPAIGN

4.4.1 LAMPAS Count Rates

Figures 4.1 and 4.2 illustrate monitoring that took place over two separate periods when the air masses were classed as polluted, originating from the south-east after crossing the highly populated suburbs of London and industrial northern Germany, as depicted by the 5-day air mass back trajectories in Figure 4.4. Both Figures 4.1 and 4.2 show the particle count rate of the LAMPAS compared with the hourly ion concentrations analysed in PM$_{10}$ samples collected by a Partisol. The LAMPAS has to be set to a specific particle size, indicated by the colour bars in Figure 4.1. It should be noted that the fluctuations in count rate of the LAMPAS can not be used directly as a measure of particle concentration due to the changing particle sizes being monitored that will effect the detection efficiency and the inlet transmission efficiency; for example a drop in count rate occurs when detecting 1.5 and 2.0 µm particles compared to the more abundant smaller particles. The count rate plots are merely used to aid selection of the data that can be used to assess changes in particle composition over time. This type of aid is required as it is thought that at least 200 spectra per hour are needed to represent a statistically significant proportion of the particles present.
Figure 4.1. The PM$_{10}$ ion concentrations and the LAMPAS count rate for 24 hours ending at 1100h BST 26/06/99.
Figure 4.2. The PM$_{10}$ ion concentrations and the LAMPAS count rate for 24 hours ending at 2300h BST 09/07/99.

Figure 4.3 details the intensive period when a clean air mass arrived in Birmingham after crossing the Atlantic Ocean and then crossing the southwest of the UK as depicted in air mass back trajectories in Figure 4.4e. The LAMPAS count rates are considerably lower primarily due to problems encountered in the field but may also be influenced by the smaller numbers of particles present in the atmosphere as well as the LAMPAS being unable to desorb/ionise
cleaner particles as demonstrated through laboratory tests using pure ammonium sulphate and sodium chloride.

Figure 4.3. The LAMPAS count rate for 10 hours ending at 1330h BST 01/07/99.
Figure 4.4. Examples of the 5-day back trajectories for air masses arriving at the receptor during the intensive monitoring periods.

a) 1200 hours BST 25/06/99

b) 0600 hours BST 26/07/99

c) 0000 hours BST 09/07/99
4.4.2 Hourly Averages

The LAMPAS count rate given in Figure 4.1 depicts five hourly episodes that have been identified as having particle sample populations that can be considered as statistically significant. The averages for each of these hourly samples are illustrated in Figure 4.5. In all cases the positive spectra are dominated by strong sodium and potassium signals due to the higher sensitivity of the nitrogen laser to these ions leading to a loss of detail in the positive spectra. To help rectify this situation each figure shows an enlarged plot of the average positive spectrum that magnifies the detail below an intensity of 100. By doing so the presence of regular $C_n$ series can now be seen along with peaks at $m/z = 7, 18, 27, 43$ and $57$, which identify lithium, ammonium, aluminium, aluminium oxide and calcium hydroxide ions as being present in the particles.
Figure 4.5. Hourly averaged spectra for particles collected during 25-26/06/99.

(a) 12.00-13.00 BST 25/06/99

(b) 19.00-2000 BST 25/06/99

(c) 23.00-24.00 BST 25/06/99
The negative spectra all contain a varying mixture of sulphur, nitrogen and carbon containing species, as denoted by the peaks occurring at m/z = -98/-97 and -80 signifying the sulphur species HSO$_4^-$/$\text{SO}_4^{2-}$ and $\text{SO}_3^-$, m/z = -62 and –46 illustrating the nitrates NO$_3^-$ and NO$_2^-$, together with the carbon series, C$_n^-$ occurring at multiples of 12, ie. m/z = 12, 24, 36…..etc.

Although the average spectra give a reasonable interpretation of the type of ions present in particles at any one hour, they do not provide evidence of whether these ions are segregated in such a way to produce only sulphur containing or only nitrogen containing particles or whether a mixture of ions occur in all particles. In other words are these particles internally or externally mixed? Evidence of any mixing can be ascertained by inspecting the individual spectra that produce each hourly average. In Figure 4.6, examples of single spectra occurring between 1200-1300h are shown. The spectra (Figures 4.6a-d) illustrate four typical major spectral patterns that have been seen to arise during this time period.
Figure 4.6. Four major spectral patterns occurring 1200-1300h 25/06/99.

(a)
Mixed Nitrate and Sulphate
25/06/99 12:07:12

(b)
Dominant Nitrate
25/06/99 12:18:26
Each of these has been classified according to the predominant ions that appear in the spectrum, for example Figure 4.6c gives an example of the highly populated elemental carbon class whose spectra are dominated by strong C$_n^-$ chains. Commonly these particles also contain other species such as NO$_2^-$ and NO$_3^-$ but at reduced intensities. Another prime example of the extent of internal mixing can be seen in Figure 4.6a. These particles have been designated as mixed sulphate and nitrates as all spectra contain intense nitrate and
sulphate signals. It has also been noted that a number of spectra occur that contain a very dominant signal at m/z = -26 which is thought to represent the species CN⁻ (see Figure 4.6b). Frequently, these particles contain the other nitrogen species NO₂⁻ and NO₃²⁻ and on occasions short Cₙ⁻ series but at reduced intensities.

4.5 OBSERVATIONS

4.5.1 Comparison between Air Masses

During the summer PUMA campaign, intensive monitoring took place to compare the change in aerosol composition between clean and polluted air masses. Throughout these periods size segregated bulk aerosol data run by research colleagues was collected alongside the LAMPAS. Figures 4.1 to 4.3 show the intensives when monitoring took place. The equivalent back trajectories shown in Figures 4.4a to 4.4e illustrate the air masses arriving at the receptor site during these episodes. The advection of these dirtier air masses was also reflected in the raised concentrations of PM₁₀ and pollutant gases, such as the PM₁₀ data gained from measurements taken from a TEOM, shown in Figure 4.7.

Figure 4.7. The variation PM₁₀ mass concentrations between 23/06/99 and 29/06/99.
Figure 4.8 represents hourly averaged spectra when a clean air mass arrived at the receptor site after passing over the Atlantic Ocean and approaching Birmingham from the southwest. Similarities between Figures 4.8a and 4.8b arise due to a dominant C_n series in the negative and large sodium signals in the positive. Differences between the two hours are also observed with stronger trace metal ion signals arising at m/z = 27, 40 and 56 in Figure 4.8a, representing aluminium, calcium and iron. This indicates that a greater proportion of particulates collected at the site in the morning hours can be attributed to crustal origins. Past studies have often used the presence of these elements as crustal tracers. If these spectra are compared to those in Figure 4.5, which can be regarded as from a dirty airmass, then an apparent increase in the carbon content of the clean aerosol can be seen. Due to the LAMPAS technique not being quantitative it is difficult to say whether this observation is a result of an actual increase in carbon containing aerosol or whether it merely reflects the reduction in the more aged aerosols that were seen during polluted episodes as in Figure 4.5. It is highly likely that this phenomenon is simply due to the diluting effects of the polluted air mass that brings with it more nitrate containing particles that will readily absorb light at 337 nm and hence be ionised in the LAMPAS. Alternatively, local emissions of carbonaceous aerosol in Birmingham may be influential.

During the arrival of clean air to the receptor site, the ratio of the Na peak to the K peak showed substantial Na enrichment from an average ratio of 0.39 during polluted episodes to 1.12 for clean episodes. Similar on-line analysis using a unipolar LAMS technique (laser ablation mass spectrometer) found that the population of a K dominated class rose considerably during periods of high particulate levels (Tan et al., 2002). Various bulk studies have suggested biomass burning as a dominant source of K at urban and background sites (Ye et al., 2003; Raveendran et al., 1995), but this is unlikely in the UK. The presence of potassium in more aged particles has also been observed by Teinila et al. (2003) where a strong correlation between the anthropogenic tracers nss-SO_{4}^{2-}, NH_{4}^{+}, NO_{3}^{-}, oxalate and nss-
K⁺ was seen. Another notable feature of this data is the presence of ammonium at m/z = 18 in Figure 4.8a. Although this peak is small compared to the other peaks present its presence still has significance in terms of its occurrence in all the polluted hourly averages compared to only 2 out of the 7 hourly clean averages measured and the low sensitivity of the LAMPAS to this ion. This complements the observation of a rise in ammonium levels seen during polluted episodes in the bulk samples.

Figure 4.8. Hourly average spectra collected when a “clean” air mass arrived at the receptor site.

(a) 0700-0800 BST 01/07/99

(b) 1200-1300 BST 01/07/99
Past studies concerning the relationship of nitrate particles with meteorological conditions have shown that under clean atmospheric conditions nearly 100% of the nitrate was found in the coarse mode, whereas during more polluted times only 40 – 60% was found as coarse nitrate (Yeatman et al., 2001). The bulk data collected in this campaign by Tilling (PhD thesis, University of Birmingham) has also demonstrated to an extent that very low fine mode nitrate levels are associated with clean air masses. The reduction of nitrates in the finer fraction can also be seen in the single particle mass spectra as shown by Figures 4.8a and 4.8b representing 0.5 μm particles. Both of these datasets have sharp qualitative decreases in the NO₂⁻ and NO₃⁻ peaks compared to the averaged spectra gained during the more polluted times in Figure 4.5a to 4.5e. In this case it is expected that the fine nitrate is associated with ammonium nitrate formed by the reaction of ammonia with nitric acid. It is therefore not surprising to observe an ammonium signal at m/z = 18 in average spectra given in Figure 4.5.

4.5.2 Fuzzy Clustering Results

Due to the extremely time consuming nature of classifying each individual particle by inspection, a fuzzy clustering process has been developed based on the fuzzy-c-means algorithm. Prior to classification mass spectra were pre-sorted according to particle size and time of collection with at least 150 spectra used in each classification run. The software designated between 5 to 10 categories for each classification and assigned each spectrum to one or more of these. Mean chemical classes were plotted for each of the classes, a number of which were very similar, usually resulting from a calibration drift. After manual inspection the drifted classes could be merged with classes that had been correctly calibrated generating 7 discrete classes. Figure 4.9 illustrates the typical mean classes that were produced. These classes included carbon containing particles with different mixtures of inorganic salts, and nitrogen and sulphur-rich inorganic particles with varying degrees of nitrate and sulphate.
Figure 4.9. An example of the seven particle classes identified through the fuzzy clustering software during the Summer PUMA campaign.

a) Elemental Carbon

b) Aged Carbon 1

c) Aged Carbon 2

d) Carbonaceous Inorganic Salt
mixing. Again these mean classes give a good representation of the amount of internal mixing occurring in different particle types.
On comparing these mean classes to the single spectra illustrated in Figure 4.6 it is very encouraging to find that it is a fairly simple process to manually classify these particles into their equivalent mean class. For example, the mixed nitrate and sulphate spectrum in Figure 4.6a would be a relatively strong member of the inorganic salt class given in Figure 4.9c, whereas the carbon series in Figure 4.6c almost certainly belongs to the Mineral and Inorganic class shown in Figure 4.9e. This provides evidence that the fuzzy classes produced are a realistic grouping of the individual spectra. The only drawback concerning these clusters arises due to the lack of information recorded in the positive spectra. This resulted from lower sensitivity settings applied to the positive signals compared to the negative signals. It therefore seems likely these clusters have been identified based mainly on the more intense negative ion spectral patterns. The spectral patterns represented by Figures 4.9a and b illustrate particles with very high carbon content. If the lack of C\textsubscript{n} series in the positive is disregarded, Figure 4.9a can be classed as typical elemental carbon. Figure 4.9b on the other hand shows a degree of internal mixing due to the higher nitrogen content (CN\textsuperscript{-} at m/z = -26, NO\textsubscript{2}\textsuperscript{-} at m/z = -46 and NO\textsubscript{3}\textsuperscript{-} at m/z = -62) that is more indicative of an aged carbon. Research carried out by Vögt et al. has shown that the presence of strong carbon series is very characteristic of particles sampled from a diesel car with the LAMPAS-2 (Vogt et al., in press). Figure 4.9c also shows a class has a clear organic origin, but increased nitrogen content confirmed by the CN\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} peaks. The particles in this class differ from those in Figure 4.9b due to the intense CN\textsuperscript{-} peak. This peak was very characteristic of a high proportion of particles in this dataset and as yet its true source has not been established though it has been suggested that it results from the presence of heterocyclic systems including C=N bonds. This class of spectra has been designated as mixed organic and salt. The spectral classes in Figures 4.9b and c may well result from atmospheric condensation and coagulation processes taking place between locally emitted diesel particles and long-range transported ammonium sulphate and nitrate aerosols.
Figures 4.9d and 4.9e represent particles with mainly inorganic characteristics shown by the combination of sulphate and nitrate peaks ($\text{NO}_3^-$ at m/z = -62 and $\text{SO}_4^{2-}$ at m/z=-97). Figure 4.9d differs from 4.9e by an increase in carbon content indicated by the presence of the dominant CN$^-$ peak at m/z=-26. Figure 4.9e has additional peaks in the positive at m/z = 7 ($\text{Li}^+$), m/z = 27 ($\text{Al}^+$), m/z = 56 ($\text{Fe}^+$) and m/z = 64 ($\text{TiO}^+$) and also a fairly strong peak at m/z = -88 representing FeO$^-$. These peaks are typical of particles from mineral origins.

The final two classes are referred to as nitrogen and sulphur rich, with each class being dominated by $\text{NO}_3^-$ at m/z = -62 and $\text{HSO}_4^-$ at m/z = -97, respectively. A characteristic feature in both these classes is the presence of peaks at high m/z ratios. In the case of the nitrate class large nitrate clusters are observed at m/z = -125 for the species $\text{HNO}_3:\text{NO}_3^-$. The higher peak at m/z = -164 has yet to be assigned. Similarly for m/z = -234, which occurs in the sulphate rich category, assignment has yet to be made.

Interpretation of this data using the fuzzy clustering method has concentrated on the spectra collected throughout the pollution episode on 25$^{th}$ and 26$^{th}$ June as well as a number of measurements taken during the day leading up to this episode. Air mass back trajectories for 24$^{th}$ June show that air arriving at the receptor site had approached from the less industrial south-west of the UK (Figure 4.3a) and therefore can be considered as clean. On comparing the back trajectories in Figure 4.3a to those given in Figure 4.3b an abrupt change in the approach of the air mass is initially seen at midnight on 26$^{th}$ June, when the air mass spent a considerable amount of time crossing the UK from the north before approaching Birmingham from the south east. A dramatic change in particle composition was also observed between the clean and dirty air masses as illustrated in Figure 4.10. Thirty-three percent of the
particles detected when clean air arrived from the southwest were categorised as elemental carbon compared to only 12% of particles detected during the more polluted time.

Figure 4.10. Change in PM$_1$ relative composition of particles by LAMPAS when the air mass arriving at the receptor site had passed over the north or the southwest of the UK.

This confirms the previous hourly average observation when an increase in the relative amount of carbon series was noted during the arrival of the clean air mass. Recent research has attributed the elemental carbon class as originating from diesel exhaust (Vogt et al., in press) although whilst other local sources such as road dust, and tyre particles are also possible, combustion sources are probably dominant. Interestingly an increase in the mineral inorganic class is also observed during the arrival of the mass from the southwest. This indicates an increase in the mineral content of the particles being detected. Possible sources of this particle type are from the resuspension of soil or road dust, both of which are likely to be of a more local origin. The most notable difference in composition between the two air masses arises in the nitrogen and sulphur rich classes. When the air mass arrived from the southwest no sulphur rich particles were detected compared to 18% of particles during the pollution episode. Similarly, a dramatic increase in nitrogen rich particles was observed when the air mass arrived from a northerly direction. Table 4.1 highlights the change in population of each of the 7 class types as the air mass arriving in Birmingham changes from clean to dirty. The table illustrates how the growth in nitrogen and sulphur rich particles was accompanied by a decrease in elemental carbon particles as the mass became increasingly
polluted with the maximum in nitrogen rich particles coinciding with the maximum concentration of nitrate ions as measured by the Partisol in Figure 4.1.

Table 4.1. Variation in the classes observed at the receptor site during a pollution episode in the Summer PUMA campaign (in percentages).

<table>
<thead>
<tr>
<th>Start Time</th>
<th>Stop Time</th>
<th>Total No. Spectra</th>
<th>Elemental Carbon</th>
<th>Aged Carbon1</th>
<th>Aged Carbon 2</th>
<th>Nitrate rich</th>
<th>Carbonaceous Inorganic</th>
<th>Mineral + Inorganic</th>
<th>Sulphate rich</th>
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</thead>
<tbody>
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<td>6/24/99 14:09</td>
<td>6/24/99 14:28</td>
<td>188</td>
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<td>10.6</td>
<td>7</td>
<td>40.3</td>
<td>7.6</td>
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</tr>
<tr>
<td>6/24/99 14:35</td>
<td>6/24/99 15:20</td>
<td>132</td>
<td>23.2</td>
<td>22</td>
<td>7</td>
<td>40.3</td>
<td>7.6</td>
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<td></td>
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<td>185</td>
<td>9.2</td>
<td>3.8</td>
<td>20</td>
<td>20</td>
<td>9.7</td>
<td>37.3</td>
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<td>6/26/99 1:47</td>
<td>373</td>
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<td>2.1</td>
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<tr>
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<td>6/26/99 4:40</td>
<td>310</td>
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<td>6.5</td>
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<td>13.3</td>
<td>45.3</td>
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<td>6/26/99 6:12</td>
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<td>7.7</td>
<td>8.3</td>
<td>16.6</td>
<td>45.3</td>
<td>22.2</td>
<td></td>
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<tr>
<td>6/26/99 10:56</td>
<td>6/26/99 11:43</td>
<td>330</td>
<td>41.4</td>
<td>10</td>
<td>22</td>
<td>17.6</td>
<td>8.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.6 WINTER PUMA CAMPAIGNS

4.6.1 LAMPAS Count Rates

During the winter PUMA campaign the LAMPAS took part in one intensive monitoring period. Throughout this period the air mass arriving at the receptor site approached from the northeast after passing over the northern conurbations and industrial areas of Northumbria and the East Midlands. The back trajectories for 1200h on 25/01/00 and 0000h on 26/01/00 plotted in Figure 4.11 illustrate the air mass passage during the previous five days.

Figure 4.11. Examples of the 5-day back trajectories for air masses arriving at the receptor during an intensive monitoring period.

a) 1200h GMT 25/01/00
Figure 4.12. The PM$_{10}$ ion concentrations and the LAMPAS count rate for 24 hours ending at 1300h BST 26/01/00.
The variation in count rate of the LAMPAS during this pollution episode is described in Figure 4.12 along with the Partisol ion concentrations. As seen with the summer data a large variation in count rate is observed. This is exemplified by a sudden decrease when the delay time is set to detect the coarse 2 µm particles. Under these conditions the average count rate becomes 1.5 counts per minute compared to 8.7 counts per minute for 0.5 µm particles over the same 24 hour period.

It should also be noted that the magnitude of the x-axis for the LAMPAS count rate during the winter campaign has increased by approximately a factor of 2. An increase in the PM$_{10}$ concentration is also seen reflecting the well-characterised phenomenon of a lowering of the boundary layer top during the winter brought about by the reduction of convection, which therefore allows more stable and less dilute conditions to prevail. The increased count rate is extremely advantageous for analysing the LAMPAS data as more confidence in sampling a statistically significant proportion of the population can be assumed when comparing any changes in overall particle composition between different hourly samples.

### 4.6.2 Hourly Averages

Figure 4.13 depicts examples of five hourly averaged spectra. Each spectrum comprises on average over 300 individual spectra, with a maximum of 912 spectra collected for the hour until 2300 hours GMT. As before, the positive spectra were dominated by very intense sodium and potassium cations at m/z = 23 and 39, respectively. For this reason the positive spectra have been enlarged so that the detail of the smaller positive peaks with intensities lower than 100 units can be seen more clearly. During each hour a number of spectra were found to consist of positive peaks only. In these cases only potassium and sodium signals occurred. Other positive peaks that are seen regularly in the positive spectra include long C$_n$ series, the minimum being C$_2^-$ at m/z = 24 and the maximum representing C$_{10}^-$ at m/z = 240. The individual spectra indicate that carbon series occur in a number of different chemical
environments. Figures 4.14a to 4.14c illustrate some typical examples of these environments, the first (Figure 4.14a) shows a clear elemental carbon chain with strong peaks in the both the positive and negative spectra. What distinguishes this carbon pattern from the others is the lack of nitrogen species at m/z = -46 and -62, signals that are clearly apparent in Figures 4.14b and 4.14c. In fact the additional peaks arising in Figures 4.14b and 4.14c, such as ammonium, potassium and nitrogen containing species, indicate the occurrence of aging processes of the pure elemental carbon species through condensation or coagulation mechanisms.
Figure 4.13. Hourly averaged spectra for particles collected during 25-26/01/00.

a) 1400-1500 GMT on 25/01/00

b) 1900-2000 GMT on 25/01/00

c) 2200-2300 GMT on 25/01/00
The hourly averages show that lithium and iron at m/z = 7 and 56, respectively occur regularly in the positive spectra. When individual spectra are inspected combinations of lithium, iron, sodium and potassium occur. In the negative spectra strong nitrogen containing peaks are seen and sometimes peaks at m/z = -88 and -104 representing the iron oxides FeO$_2^-$ and FeO$_3^-$. The phosphorus species PO$_2^-$ and PO$_3^-$ have also been detected at m/z = -63 and –79. Figure 4.14d illustrates a spectrum combining all these peaks. Fingerprinting has suggested that a possible sources for this type of particle include soil or road dust. The crustal origin of this type of particle is reinforced by the presence of silicon oxides, SiO$_2^-$ and SiO$_3^-$ at m/z = -60 and –76. Although this kind of spectrum is interesting its occurrence appears to be rare in this environment.
Figure 4.14. Examples of individual spectra collected during 25/01/00.
The negative averaged spectra contain intense signals at m/z = -46, -62 and -97 indicating the presence of the nitrogen and sulphur containing species, NO$_2^-$, NO$_3^-$ and HSO$_4^-$. Once more when the individual spectra are investigated, a mixture of spectral patterns containing these peaks are seen. Figures 4.14e to 4.14g illustrate examples of the most dominant patterns observed. Figure 4.14e represents particles whose major constituent is nitrate. It is usual to observe NO$_2^-$ and NO$_3^-$ as the dominant nitrogen species in most spectra but sometimes a peak at m/z = -26 indicating CN$^-$ is also observed as in Figure 4.14g. On these occasions other carbon peaks are usually also seen. It should also be noted that other spectra also contain these sulphur and nitrogen containing species but they are not the most dominant feature, for example in Figures 4.14b to 4.14d.

The kind of detail that is seen in individual spectra such as the mineral salt spectrum in Figure 4.14d highlights the weaknesses experienced when using hourly averages to probe the data. For instance the presence of a peak at m/z = -60 coincides with both the C$_5^-$ and SiO$_2^-$ species. By using the hourly averages it is not possible to conclude how many spectra can be attributed to each species. However, the averages do indicate that most of these m/z = -60 peaks are most probably due to the C$_5^-$ as other C$_n^-$ peaks occur more intensely than the alternative SiO$_2^-$ species at m/z = -76, but only by inspecting each individual particle for the correct peak combinations can one be completely certain.

4.6.3 Observations

The hourly averaged spectra suggest that the overall composition of particles did not change dramatically throughout the pollution episode. This observation gains support from the PM$_{10}$ ion concentrations in Figure 4.12. In this case the levels of chloride, sulphate and ammonium all follow similar trends. The only divergence is seen in the nitrate ion whose concentration shows a dramatic change occurring around 2030 hours, and peaking at 0330 hours on
26/01/00. The mass distribution illustrated in Figure 4.15 shows that the nitrate distribution is bimodal with a major peak in the fine between 0.4 – 0.5 µm and a coarse peak occurring around 2 – 3 µm. Using the assumption that during polluted times 40 – 60% of nitrate is found in the fine mode (Yeatman et al., 2001), a change in the number of nitrate containing species detected by the LAMPAS should be observed. This prediction is not borne out by the averaged spectra.

Figure 4.15. PM$_{15}$ mass distribution for 12 hours ending at 1200h GMT 26/01/00

To be able to scrutinise the data in more detail it is necessary to attempt to categorise each particle depending on the peaks present. Using some of the spectra in Figure 4.14 as models for typical spectral patterns, the criteria in Table 4.2 were used to categorise each spectrum. Only a select number of important peaks were used in this process. These were chosen depending on their occurrence and to complement the bulk data. For example, the peaks that are characteristic of the mineral category were not used as they do not occur on a regular basis. The criteria selected also ensured that each spectrum could only be categorised once. As a result, it was not possible to include chloride in this process as it was always found to occur in combination with other peaks. In the majority of cases no criterion was allocated to the sodium or potassium peaks. In other words, it did not matter if the classified spectra had
either of these peaks present or not. This decision was taken because no rationale has been established for the presence of these peaks and their occurrence seems to be dominant in nearly all sources. The instrument shows exceptional sensitivity towards these elements.

Figure 4.16 illustrates the results of this procedure. The most notable feature is the dominance of the sodium and/or potassium rich spectra. These spectra do not contain any other major peaks such as nitrates, sulphates or carbon. It is difficult to give a valid reason behind this observation but as noted above the instrument is particularly sensitive to both elements.

| Table 4.2. Selection criteria for categorising spectra. |
|-----------------------------|=============|=============|=============|=============| 18 | 23 | 39 |
| Category                     | Mass to charge ratio | Category | \(-97\) | \(-72\) | \(-62\) | \(-48\) | \(-46\) | 18 | 23 | 39 |
| Nitrate only                 | N            | N            | Y            | N            | Y            | N            | O            | O  |       |
| Sulphate only                | Y            | N            | N            | N            | N            | N            | O            | O  |       |
| Elemental carbon             | N            | Y            | N            | Y            | N            | N            | O            | O  |       |
| Secondary                    | O            | O            | O            | O            | O            | Y            | O            | O  |       |
| Mixed nitrate/sulphate       | Y            | N            | Y            | N            | Y            | N            | O            | O  |       |
| Sodium/potassium only        | N            | N            | N            | N            | N            | N            | Y            | Y  |       |
| Aged carbon                  | O            | Y            | O            | Y            | O            | N            | O            | O  |       |

Key: N = peak must not be present, Y = peak must be present, O = No criteria

Figure 4.16. PM\(_1\) composition of particles collected by the LAMPAS.
Other major classes include the aged carbon and mixed nitrate and sulphate groups. The observation of more aged aerosols is thought to provide evidence of secondary production processes having occurred. This is not surprising as secondary processes are traditionally indicative of long-range transport. The mass size distribution in Figure 4.15 reflects the presence of secondary components by the large ammonium peak in the fine aerosol region. It also confirms the presence of sulphate and nitrate occurring together in fine particles due to the coinciding peaks between 0.4 and 0.5 µm. In the single particle data ammonium is not easily detected due to low sensitivity and therefore many of these aged aerosols will not have been seen to contain ammonium.

The occurrence of pure nitrate and pure sulphate classes should also be noted. These spectral patterns are seen often throughout the pollution episode with nitrate generally being the dominant of the two. The fact that these classes do not show internal mixing may suggest that they have not had enough time to participate in secondary inter-conversions processes. Recent literature has suggested that nitrate formation can also occur via local sources, which may go some way to explain this phenomenon (Tilling, 2002).

4.6.4 Fuzzy Clustering

Fuzzy clustering of the data was carried out in a similar manner to the summer data, which is described in section 4.5.2. For the winter data eight fuzzy classes were generated all of which are presented in Figure 4.17. Some of these classes are comparable to those generated for the summer campaign, for example on both occasions an elemental and aged carbon class occurred. In the case of the winter data, both carbon categories contained fairly strong positive series. The increase in positive signal intensities for the winter spectra compared to those obtained during the summer is an artefact of the attenuation settings that were applied prior to collection.
Generally, the winter classes range from spectra that have high concentrations of inorganic species such as nitrogen and sulphur to highly mixed species with organic and inorganic constituents. Two carbon rich classes were also generated illustrated by Figures 4.17a and 4.17b. Figure 4.17a has been given the label elemental carbon as it represents particles that are highly carbon enriched but have not undergone any degree of secondary processes.

Figure 4.17. Examples of the eight particle classes generated through the fuzzy clustering software during the Winter PUMA campaign.

- **a) Elemental Carbon**
- **b) Aged Carbon**
- **c) Carbonaceous Inorganic**
- **d) Nitrate Rich**
Figure 4.7 continued.

- e) Sulphate Rich
- f) Mixed Inorganic Salt
- g) Sodium Rich Salt
- h) Potassium Rich Salt
This is demonstrated by the lack of inorganic constituents such as NO\textsubscript{2} and CN\textsuperscript{-} that can be seen far more clearly in Figure 4.17b. Figure 4.17b also has a strong ammonium peak present at m/z = 18, which again illustrates that these spectra originate from particles that have secondary characteristics. As suggested previously in Section 4.5.2 both carbon rich cases can be traced back to diesel emitted particulates as demonstrated by lab work carried out by Vogt and co-workers (Vogt et al, in press). This work has also demonstrated that other long carbon chain series can also occur via sources such as brake dust and tyre particles. A notable trait of these two classes is a reduction in the sodium and potassium signals that feature regularly in the other classes. Figure 4.17c illustrates another carbon containing cluster that is extremely different to the elemental and aged carbon classes. In this example the inorganic elements are more than comparable to the organic carbon chains, which can be seen in the positive and negative spectrum. Strong Na\textsuperscript{+} and K\textsuperscript{+} peaks dominate the positive indicating that these particles have most probably been formed in a different manner. Such mechanisms include the condensation of semi-volatile organic species onto inorganic particulate surfaces. The presence of Li\textsuperscript{+} and Fe\textsuperscript{2+} is characteristic of mineral species.

Figures 4.17d to 4.17f depict the three major inorganic salt classes that split into nitrate rich, sulphate rich and mixed nitrate and sulphate types. The nitrate rich class in Figure 4.17d has a characteristic NO\textsubscript{3}\textsuperscript{-} peak at m/z = -62, along with a smaller peak at m/z = -46 representing the NO\textsubscript{2}\textsuperscript{-} species. Sulphate also occurs in these particles indicated by mass to charge ratios, m/z = -80 and -97, but the intensity of each is considerably weaker than the NO\textsubscript{3}\textsuperscript{-} peak. Similar comments can be made for the sulphate rich class (Figure 4.17e) with nitrogen and sulphur species both being present but this time the HSO\textsubscript{4}\textsuperscript{-} peak is dominant. Figure 4.17f appears to be an average between these two extremes and represents particles that have undergone more mixing. The final two classes have been designated as sodium rich and potassium rich salts according the major Na\textsuperscript{+} and K\textsuperscript{+} peaks, respectively. Following the results of Section 4.6.3 it
is not surprising to find classes incorporating these two elements. Possible sources of sodium include sea-salt or salt from road de-icing activities. Potassium sources include wood combustion, sea salt and clay minerals.

The population of each for each of the fuzzy clusters during the entire pollution episode for PM$_1$ is shown in Figure 4.18.

**Figure 4.18.** Composition of PM$_1$ derived via fuzzy clustering technique during an intensive monitoring period when the air mass arriving at the receptor site had approached from the North East.

![Pie chart showing the composition of PM$_1$](image)

**Total particle number = 5532**

The most extraordinary feature of Figure 4.18 is the high abundance of the potassium rich category that represents 1826 of the particles collected. This is a very surprising result as previous bulk data measurements in Birmingham have shown that potassium usually represents relatively small proportion of the total particulate concentration. Therefore, caution must be used when interpreting this result as effects such as instrument relative sensitivity leads to overestimation of the K and Na classes. The results in Section 4.6.3 using a different method indicated that pure Na and K particles represented a total of 22% of the PM$_1$ composition. The other (24%) potassium and sodium rich particles must also contain other constituents. It has been observed by inspection of the remaining spectra that it is
It is possible to classify them into the inorganic and organic classes depending on their negative spectral pattern. It seems that the fuzzy clustering method has not taken into account the detail of the negative spectra but instead the dominant K⁺ signal has been the only influencing factor in the fuzzy clustering process.

The second most populated class is the sulphate rich category although interestingly Figure 4.16 showed that pure sulphate particles were not the dominant species and the sulphate only particles accounted for only 220 spectra. This implies that the remaining 1052 spectra in the fuzzy sulphate rich category must contain mixed spectra with intense sulphate peaks. The presence of sulphate rich PM₁ during pollution episodes is not surprising as it is known as a long range transported pollutant. Possible sources include the transformation of SO₂ emitted from coal-fired power stations a number of which lie to the north east of Birmingham.

4.6.5 **Seasonal Inter-Comparison**

Fuzzy clustering results confirm that the composition of particles in each pollution episode is very different. No potassium or sodium rich class was observed in the summer campaign, which was primarily an effect of the change in attenuation settings between the two campaigns, but may also reflect changing atmospheric composition caused by increased de-icing activities and combustion sources. A related observation is that the occurrence of chloride at m/z = -35 is not seen in as readily in the summer data. For example, if the summer averaged spectra are compared to the winter averages, a fairly strong Cl⁻ peak is seen regularly in winter compared to hardly at all during the summer. MOUDI results showed chloride as having the greatest inter-seasonal variation probably due mainly to coarse sea salt, although the mass size distribution in Figure 4.15 depicts small amounts of chloride in the PM₁ range. This is confirmed by the chloride occurrence in the fine particles sampled by the LAMPAS. The increased observations of fine chloride and sodium may have arisen due to the transport
of sea-salt aerosol from coastal regions. This is consistent with the concept of high wind
speeds encountered during the winter being responsible for efficient bubble bursting
mechanisms that release NaCl aerosol from the sea.

During both winter and summer episodes sulphate rich particles accounted for a high
percentage of PM$_1$. The spectral pattern for each period was almost identical giving reason to
believe that the compositions of the sulphate rich particles were very similar. Conversely, a
large difference in population of nitrate rich particles was observed with these accounting for
over 34% of the PM$_1$ concentration in summer compared to only 7% during the winter
episode. This seasonal observation is contrary to data collected by the MOUDI, which
indicated that formation of nitrate was enhanced during the winter due to the effects of
temperature and humidity on the ammonium nitrate dissociation equilibrium. The observed
higher abundance of nitrate-rich species in the summer campaign can be attributed to the
different routes taken by the air masses to our site. For example, during the summer episode
the air mass passed over the north of the UK before looping out over continental Europe and
traversing over the highly populated London area (Figure 4.11), allow additional NO$_x$ to be
picked up and converted into particulate nitrate before arriving at the receptor site.
5. LONDON CAMPAIGNS

5.1 INTRODUCTION

In 2001, two measurement campaigns were conducted in central London. For each campaign, measurements were located at two sites; close to a busy road (roadside site) and at a background site that was not directly influenced by traffic. The first campaign includes measurements between 14\textsuperscript{th} February to 22\textsuperscript{nd} February with at least one 24 hour measurement episode at each site. The second campaign was performed from 24\textsuperscript{th} July to 26\textsuperscript{th} July with continuous measurements made at each site. Throughout all studies information regarding the composition and size distribution of atmospheric aerosols were collected using both single particle and bulk techniques. The major aims of this work included evaluation of:

- roadside versus background composition, i.e. the traffic increment
- the influence of meteorology on particle composition in inner London
- seasonal influences on particle composition
- comparison of bulk analytical techniques with single particle mass spectrometry

5.2 SAMPLING SITES

Sampling was conducted at two sites in inner London located at Regent’s Park and Exhibition Road. The roadside site was located on Exhibition Road, adjacent to the main Imperial College campus. At this location the Ford Mobile Laboratory (FML) could be parked safely on the pavement approximately 3 metres from the road. Regent’s Park was used as an urban background site, with the closest major road, Marylebone Road, situated approximately 500 metres from the sampling site. The site could therefore could be considered as being away from any major direct traffic source. The FML was sited in the grounds of Regent’s College, with the immediate surrounding area being used as park land. The sites are shown diagramatically in Figure 5.1 and pictorially in Figure 5.2.
Figure 5.1. The two sampling sites used during the London winter campaign. The precise location of sampling is indicated by an arrow.

a) Roadside site – Imperial College, Exhibition road

b) Urban background site – Regent’s Park College, Regent’s Park
Figure 5.2. The mobile laboratory at a) Regent’s Park background site and b) Exhibition roadside site.
5.3 DATA COLLECTION

5.3.1 Winter Campaign

Sampling took place for a total of 10 days from 14\textsuperscript{th} February until 23\textsuperscript{rd} February 2001. Table 5.1 outlines the compositional and physical aerosol properties that were measured throughout this period.

<table>
<thead>
<tr>
<th>Detection of</th>
<th>Technique</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk aerosol (composition)</td>
<td>Partisol</td>
<td>4 hours</td>
</tr>
<tr>
<td></td>
<td>MOUDI</td>
<td>4 to 8 hours</td>
</tr>
<tr>
<td></td>
<td>Carbon analyser</td>
<td>3 hours</td>
</tr>
<tr>
<td>Single particle (composition)</td>
<td>LAMPAS</td>
<td>variable</td>
</tr>
<tr>
<td>Bulk aerosol (mass/surface area/volume)</td>
<td>TEOM</td>
<td>1 minute</td>
</tr>
<tr>
<td></td>
<td>APS</td>
<td>5 minutes</td>
</tr>
<tr>
<td></td>
<td>SMPS</td>
<td>7 1/2 minutes</td>
</tr>
<tr>
<td>Trace gases</td>
<td>Gas analyser for NO, NO\textsubscript{2}, O\textsubscript{3}</td>
<td>5 minutes</td>
</tr>
<tr>
<td>Humidity, temperature, wind speed/direction</td>
<td>Van met sensors</td>
<td>15 minutes</td>
</tr>
</tbody>
</table>

The measurements made with the LAMPAS are listed in Appendix I. The LAMPAS was set to measure two particle sizes, 0.7 \(\mu\)m and 2 \(\mu\)m, representing the peaks of the accumulation and coarse modes. It should be noted that a number of problems arose during the campaign, including displacement of a mirror used to focus the desorption/ionisation laser into the ionisation chamber that occurred during transportation of the FML. Care was taken to replace the mirror, but it could not be certain that the laser was still aligned perfectly, and realignment was not possible under field conditions. Another difficulty was discovered with one of the PMTs, which had a drifting baseline. Therefore, continual readjustment of the trigger level was required during particle detection.

Appendix I shows that two consecutive 24 hour measurements were made at the urban background site. This was not possible at Exhibition Road, due to a PMT failure. Monitoring continued employing only one PMT to trigger the desorption/ionisation laser.
5.3.2 **Summer Campaign**

The measurements made during the Summer 2001 London campaign are summarised in Table 5.2 below. Comparable bulk measurements were made for this campaign as during the winter period.

<table>
<thead>
<tr>
<th>Detection of</th>
<th>Technique</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk aerosol (composition)</td>
<td>Partisol</td>
<td>4 hours</td>
</tr>
<tr>
<td></td>
<td>MOUDI</td>
<td>4 to 8 hours</td>
</tr>
<tr>
<td></td>
<td>Carbon analyser</td>
<td>3 hours</td>
</tr>
<tr>
<td>Single particle (composition)</td>
<td>LAMPAS</td>
<td>variable</td>
</tr>
<tr>
<td></td>
<td>ATOFMS</td>
<td>variable</td>
</tr>
<tr>
<td>Bulk aerosol (mass/surface area/volume)</td>
<td>TEOM</td>
<td>1 minute</td>
</tr>
<tr>
<td></td>
<td>APS</td>
<td>5 minutes</td>
</tr>
<tr>
<td></td>
<td>SMPS</td>
<td>7 1/2 minutes</td>
</tr>
<tr>
<td>Trace gases</td>
<td>Gas analyser for NO, NO₂, O₃</td>
<td>5 minutes</td>
</tr>
<tr>
<td>Humidity, temperature, wind speed/direction</td>
<td>Van met station</td>
<td>15 minutes</td>
</tr>
</tbody>
</table>

Single particle data were monitored using both the LAMPAS and the ATOFMS. One 24 hour measurement period was carried out at each of the two sites, Regent’s Park and Exhibition Road. A number of technical problems arose with the LAMPAS due to the nitrogen laser being replaced by an excimer laser by Ford Research Centre only a few days prior to our taking delivery of the instrument for the campaign. Therefore, time had not been available to ensure that the instrument was in satisfactory condition for fieldwork, i.e. optical mountings were not tightened allowing them to move during transportation of the instrument. For this reason a lot of time was expended having to re-align the laser in the field, which proved very problematical. Nonetheless, satisfactory sets of data were achieved at both roadside and background sites.

5.4 **DATA ANALYSIS**

The following sections are divided so that results from the winter and summer campaigns are analysed separately. For each campaign the bulk results, along with meteorology are reviewed and the overall atmospheric conditions are summarised. Single particle data are
analysed in the light of these conditions. Similar data analysis procedures to those in Section 4 were employed including consideration of count rates, mass spectrum averages and fuzzy clustering.

5.5 London Winter Campaign Results

5.5.1 Air Mass Back Trajectories

Throughout the campaign the air mass arriving into London approached mainly from a northerly direction. Figure 5.3c shows one such trajectory, in which the air mass had passed over parts of the East Midlands but had always stayed close to the coast. Figure 5.3d shows another trajectory from a similar direction in which the air mass had spent the majority of its time travelling over the Atlantic Ocean and North Sea rather than passing over inland regions. Periods such as these indicate that the air arriving into London could be classed as clean. Towards the beginning of the campaign the air mass altered direction and approached from the southeast. The back trajectory in Figure 5.3a shows that the air spent a considerable amount of time passing over northern Europe including the industrial areas of northern Germany. It might reasonably be assumed that the air mass arriving into London during this period is likely to be heavily polluted.

5.5.2 Bulk Chemical Data and Particle Size Distributions

Table 5.1 gives a summary of the techniques and time resolution adopted for resolving the chemical and physical properties of atmospheric aerosols. The results of the analysis of this data are summarised below.

5.5.2.1 Partisol data

Figure 5.4 represents the mean aerosol composition at the roadside and background determined from the Partisol samples. A statistical summary for the particulate anions is
shown in Table 5.3. These values are comparable to concentrations of the same anions, \( \text{NH}_4^+ \), \( \text{Cl}^- \), \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) in PM\(_{10}\) measured in previous studies, such those conducted at an urban site in Basel, Switzerland during winter where average concentrations were 2.35, 0.26, 5.50 and 4.30 \( \mu \text{g.m}^{-3} \) respectively (Roosli et al., 2001). In this study elevated levels of sulphate were found in London at the background site, most probably attributable to the influx of long-range pollutants.

<table>
<thead>
<tr>
<th>Site</th>
<th>Coarse</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{NH}_4^+ ) (( \mu \text{g m}^{-3} ))</td>
<td>( \text{Cl}^- ) (( \mu \text{g m}^{-3} ))</td>
</tr>
<tr>
<td>Background</td>
<td>average 0.34 0.28 0.93 0.21 2.46 0.17 2.11 5.15</td>
<td>Min 0.00 0.11 0.02 0.00 0.20 0.14 0.45 1.12</td>
</tr>
<tr>
<td></td>
<td>Max 1.61 0.67 2.51 0.83 6.09 0.66 6.78 13.19</td>
<td>sd 0.45 0.22 0.70 0.31 1.95 0.13 1.85 3.95</td>
</tr>
<tr>
<td>Roadside</td>
<td>average 0.89 1.08 1.23 0.48 1.65 0.89 2.31 4.17</td>
<td>Min 0.00 0.11 0.88 0.22 0.29 0.14 0.97 3.08</td>
</tr>
<tr>
<td></td>
<td>Max 2.86 2.15 1.87 1.21 4.17 5.41 4.20 6.34</td>
<td>sd 1.14 0.85 0.36 0.33 1.39 1.99 1.13 1.08</td>
</tr>
</tbody>
</table>

Table 5.3. Averages, minimum, maximum and standard deviation of particulate \( \text{NH}_4^+ \), \( \text{Cl}^- \), \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) at two sites in London (winter 2001).
Figure 5.3. Examples of 5 day air mass back trajectories for air masses arriving at the London sampling sites.

a) 0000 hours GMT 15/02/01

b) 1200 hours GMT 15/02/01

c) 1200 hours GMT 16/02/01
d) 0000 hours GMT 17/02/01

![Map Image]

e) 0000 hours GMT 20/02/01

![Map Image]

f) 1200 hours GMT 20/02/01

![Map Image]
g) 0000 hours GMT 21/02/01

h) 1200 hours GMT 21/02/01
Figure 5.4  Aerosol mean composition for major anions determined from analysis of Partisol samples.

a) Coarse Background

b) Fine Background

c) Coarse Roadside
d) Fine Roadside

Nitrate µg m$^{-3}$

Sulphate µg m$^{-3}$

Chloride µg m$^{-3}$

Ammonium µg m$^{-3}$
Figure 5.4 shows the following facets:

- sulphate and ammonium reside predominantly in the fine particles consistent with their source in long-range transport. Chloride appears mainly in the coarse particle fraction whilst nitrate, although coarser than sulphate, is distributed relatively evenly between coarse and fine particles (allowing for the higher total concentration of fine than coarse particles);
- the component showing the greatest elevation at roadside relative to the background site is chloride;
- more extensive comparisons between the two sites are not warranted since the data were not collected simultaneously. They were, however, collected concurrently with the operation of the particle mass spectrometer instruments and therefore are of value in assessing the mass spectrometric data for particles containing these species.

The composition of each individual Partisol sample is given in Appendix II.

5.5.2.2 Impactor data

Examples of the mass distributions collected with a MOUDI are given in Appendix II. These plots reveal the following observations:

- Sulphate is found predominantly in the fine mode peaking around 0.4 –0.5 μm. A smaller mode is seen in the coarse fraction.
- Ammonium follows a similar pattern to sulphate peaking in the fine with very little in the coarse fraction.
- At both the background and roadside sites nitrate is bimodal. The background site illustrates that high concentrations of coarser particles were observed in the size range 1-2 μm, that were not as abundant at the roadside site. This suggests the occurrence of different nitrate sources during this period.
• Chloride was observed at both sites. Distributions here suggest bimodality and therefore two sources of chloride arriving at the sites.

5.5.2.3  Particle size distributions and gas data

Size distributions measured with the Scanning Mobility Particle Sizer appearing in Figure 5.5 have been analysed according to the data files obtained by the LAMPAS in Appendix I (LAMPAS files indicated in legends on graph). Figure 5.5 shows a substantial temporal variation in total particle number concentration according to the date and time of sampling. The data from the Regents Park background site (Figure 5.5a) show primarily a rather well coagulated aerosol with a modal diameter typically around 70 nm diameter confirming that the main influence at the site is from general urban and long-range sources rather than local traffic. There is one sampling period (010216b) in which a mode at 20 nm diameter is suggestive of a rather local traffic influence. This may well be a result of delivery vehicles coming onto Regent’s Park College site.

In comparison, the data from the Exhibition Road roadside site show generally higher particle number concentrations (Figure 5.5b), although not by a large margin and a tendency towards a mode at diameters around 30-40 nm, slightly larger than that typically observed at the highly traffic-polluted Marylebone Road site of 25-30 nm mobility diameter. Figure 5.6 shows data from the combined SMPS and APS particle size distributions. These are suggestive of an artefact in the APS data at diameters of less than around 1000 nm and therefore the apparent peak in the surface area concentration data at around 800 nm should probably be discounted.

In Figure 5.7, the surface area size distributions are plotted according to the period of sampling. The intensity of redness in the colour corresponds to periods of high surface area at
the times indicated by the x-axis and the particle diameter indicated by the y-axis. In Figure 5.88 the carbon monoxide concentrations (red line) and NOₓ concentrations (blue line) are shown alongside a plot of the surface area data this time shown in profile as well as colour. It clearly emerges from this graph that the large peaks in the surface area distribution at sizes of less than 100 nm diameter correspond closely to peaks in the carbon monoxide and NOₓ data which are themselves generally quite closely correlated. This gives a clear indication of road traffic as being the major cause of elevation in the datasets for particulate matter as well as for the gas phase pollutants. Interestingly, the highest concentration excursions both for the gases and for particle surface area occur during the period 15-16 February when the equipment was based at Regents Park. The weather during that period was relatively stagnant and the concentrations result from a build-up of pollution across London as a whole.

5.5.2.4 Carbon analyser

Pie charts incorporating the elemental and organic carbon data appear in Figures 5.9. Elemental and organic carbon are emitted by combustion sources, especially road traffic and it is not unexpected that higher concentrations, especially for elemental carbon were observed at the roadside site, although there is an important caveat that the samples were not collected simultaneously and therefore no very direct comparison can be made. However, the fact that the sulphate concentrations were identical suggests that atmospheric conditions were relatively similar.

In Figure 5.10, the concentrations of elemental and organic carbon respectively have been plotted against simultaneously measured concentrations of NOₓ. These give intercepts of 1.9 µg m⁻³ for elemental carbon and 0.7 µg m⁻³ for organic carbon representing carbon which is not associated with NOₓ emissions and therefore unlikely to arise from road traffic.
Figure 5.5  Particle size distribution data determined from SMPS Measurements.

a) Particle size distribution for background

b) Particle size distribution for roadside
Figure 5.6  Particle size distribution data from SMPS (grey) and APS (red) measurements.

a) Background number concentration

b) Background surface area concentration

c) Roadside number concentration

d) Roadside surface area concentration
Figure 5.7. Calculated particle surface area (colour) as a function of log particle diameter and time of sampling, February 2001.
Figure 5.8. Time series of particle surface area (colour) as a function of log particle diameter, carbon monoxide and NO$_x$, February 2001.
Figure 5.9. Average aerosol composition of PM$_{10}$ at two London sites from Partisol samples and carbon analyser data.

a) Background

- Nitrate $\mu$g m$^{-3}$: 5.55
- Sulphate $\mu$g m$^{-3}$: 2.80
- Chloride $\mu$g m$^{-3}$: 3.04
- Ammonium $\mu$g m$^{-3}$: 1.32
- Organic carbon $\mu$g m$^{-3}$: 2.52
- Elemental carbon $\mu$g m$^{-3}$: 0.45

a) Roadside

- Nitrate $\mu$g m$^{-3}$: 4.78
- Sulphate $\mu$g m$^{-3}$: 3.54
- Chloride $\mu$g m$^{-3}$: 1.43
- Ammonium $\mu$g m$^{-3}$: 2.54
- Organic carbon $\mu$g m$^{-3}$: 1.97
- Elemental carbon $\mu$g m$^{-3}$: 5.64
Figure 5.10. Relationships between simultaneously measured elemental carbon and NO$_x$ and organic carbon and NO$_x$, February 2001.

a) NO$_x$ versus elemental carbon

\[
EC = 0.0349 \times NO_x + 1.9148
\]

\[R^2 = 0.7397\]

b) NO$_x$ versus organic carbon

\[
OC = 0.007 \times NO_x + 0.6836
\]

\[R^2 = 0.2572\]
5.5.3 **Single Particle Data**

5.5.3.1 **LAMPAS count rates**

Two measuring periods of approximately 24 hours each were made at the background site. The first began on 14\textsuperscript{th} February and continued through the pollution episode that has been confirmed via air mass back trajectories in Figure 5.3a and the elevated surface area concentrations in Figure 5.7. Figure 5.11 illustrates the particle detection rate of the LAMPAS at the background site and the corresponding PM\textsubscript{2.5} ion concentrations as measured by the Partisol.

![Figure 5.11](image_url)

**Figure 5.11** The PM\textsubscript{2.5} ion concentration and the LAMPAS count rate in the period ending at 1100 hours GMT on 17/02/01 at the background site.
The count rate of the LAMPAS throughout this time was very slow with a maximum count rate of 7 particles per minute being detected, and average counts around 1.5 particles per minute. This is by no means comparable to the count rates that were obtained during the winter PUMA campaign where an average count rate of about 7 particles per minute was obtained. It should also be noted that the elevated particle number concentrations indicated by the bulk data is not reflected by the LAMPAS. In a similar manner the roadside LAMPAS count rate was plotted along with the variation of Partisol concentration in Figure 5.12.

Figure 5.12  The PM$_{2.5}$ ion concentration and the LAMPAS count rate during the period ending at 1200 hours GMT on 21/02/01.
Again sampling took place over a two day period starting on 19th February, this time running for just over 36 hours. The average count rate at this site rose slightly to 2 particles per minute and again peaking at 7 particle per minute. A slight variation in count rate between coarse, 2 µm and fine, 0.5 µm particles is observed but this it not as marked as observations made with the PUMA data. These count rates indicate that the LAMPAS was not working optimally. The majority of problems were caused by drifting photomultiplier tube signals that meant the particle detection signals fell below the threshold required for the internal triggering system to recognise that a particle was present.

5.5.3.2 Comparison between roadside and background sites

Before comparing the background and roadside datasets in depth it is necessary to draw attention to the back trajectories in Figure 5.3, which depict three very different air masses. These illustrate that air masses arriving into London during the first monitoring day at Regent’s Park (Figure 5.3a) and throughout the roadside monitoring period could be classed as polluted after passing over industrial and highly populated regions. Whereas, during the second monitoring period at Regent’s Park the air mass spent the majority of time crossing the Atlantic Ocean and North Sea, therefore indicating the arrival of a much cleaner air mass. The arrival of different air masses into London makes it extremely complicated to compare the two sites and caution must be taken when interpreting the results.

Figure 5.13 illustrates the average composition of aerosol detected at the background and roadside sites. The background spectrum represents particles that were collected between 16th and 17th of February therefore eliminating the particles analysed during the extreme polluted conditions, whilst the polluted background and polluted roadside represent spectra that were collected during more polluted times. Figure 5.13 generally shows that stronger signals of all constituents were seen at the roadside site, with average intensities of the nitrogen containing
species around 1300 units at the roadside compared to relative intensities of about 500 units at the background. Apart from the differing intensity, most probably due to better absorption of laser energy when contaminants have deposited onto the surface of the particles, these spectra seem very similar in terms of the inorganic constituents such as \( \text{NO}_3^- \), \( \text{NO}_2^- \) and \( \text{HSO}_4^- \) as well as organic species (e.g., \( \text{C}_n^- \) chains). However, it is only by looking at the individual spectra that real insights are gained into how particle composition varies from site to site. Figure 5.14 depicts the results of classifying the individual spectra according to the criteria used previously in Section 4.
Figure 5.13 The average composition of particles analysed at a) the polluted background b) the background site collected between 16th and 17th February and c) the roadside site collected from the 19th to 21st February.
To verify that this classification method has been successful, spectra for each class was generated by averaging the classified individual spectra. Results of this process, given in Appendix III, indicate that the classification criteria are valid. The above results show that the sodium or potassium class along with the aged carbon class are the most abundant category of spectra at both the background and roadside sites. The nitrate- and sulphate-only classes, and the pure elemental carbon class are less abundant, indicating that more homogeneous aerosols are not as common, most probably due to the high concentration of local sources (ie. traffic) within central London. An interesting observation arises when the particle composition of the background site is compared under polluted and clean conditions. The most dramatic effect is seen in the aged carbon class indicating an increase under polluted conditions of long-range transported carbon species that have undergone heterogeneous surface reactions or condensation processes, most probably after travelling across northern Germany. The observation of ammonium-containing particles during the pollution episode should also be considered as important even though numbers of observations are still low as this demonstrates the addition of secondary aerosol during long range transport of the polluted air mass. The average plot for this class shown in Appendix III Figure d implies that these
particles are also rich in sulphate, nitrogen-containing species and carbon showing that significant coagulation and condensation processes have taken place. Significant fluctuations are also seen in the sodium or potassium-only class. For example under clean background conditions the Na/K only class dominates the aerosol composition. This feature is reduced under the more polluted background and roadside conditions indicating that this class is representative of clean aerosol. The nature of the type of sodium or potassium peaks that contribute to this trend is clarified in the following section.

Slight differences in the average spectra can also be observed in terms of the metal content. For example, small peaks at m/z = 138 and 154 occur in the roadside data that are not observed at the background site. These peaks are thought to represent barium and barium oxide, respectively and even though these peaks are small compared to other peaks present their observation is important as they are also absent in the polluted background sample, indicating that additional particle sources are present at the roadside. In this case the most probable source of these peaks is due to particles produced from the wear of brake linings and other mechanical wear of vehicle parts. A similar source can account for the peak at m/z = -88, that indicates the presence of either FeO$_2^-$ or Si$_2$O$_3^-$. Such peaks are detected more frequently amongst the roadside than background particles. Typical sources are known to include road dust or soil. The presence of these peaks near the road may well be due to the re-suspension of such particles by traffic activity. Table 5.5 gives the relative contributions of particulate metal content in percentages of total particle number found at the roadside and background sites. In comparing this data a crude assumption must be made that the two polluted air masses bring with them more comparable metal concentrations than the clean maritime air mass.
Table 5.4  Relative contribution (%) of particulate metals to the overall particle number collected with the LAMPAS at the roadside and background sites.

<table>
<thead>
<tr>
<th></th>
<th>FeO$_3^-$</th>
<th>SiO$_3^-$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>Al$^+$</th>
<th>K$^+$</th>
<th>Fe$^+$</th>
<th>Cu$^+$</th>
<th>TiO$^-$</th>
<th>Ba$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polluted Background</td>
<td>1.10</td>
<td>2.43</td>
<td>1.77</td>
<td>78.37</td>
<td>2.21</td>
<td>42.16</td>
<td>1.99</td>
<td>0.44</td>
<td>0.44</td>
<td>0.00</td>
</tr>
<tr>
<td>Clean Background</td>
<td>3.14</td>
<td>3.77</td>
<td>1.57</td>
<td>23.27</td>
<td>0.31</td>
<td>12.26</td>
<td>1.57</td>
<td>0.00</td>
<td>0.63</td>
<td>0.00</td>
</tr>
<tr>
<td>Polluted Roadside</td>
<td>13.01</td>
<td>10.84</td>
<td>1.90</td>
<td>65.04</td>
<td>1.90</td>
<td>51.90</td>
<td>5.15</td>
<td>0.68</td>
<td>0.81</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The general observations seen in the averaged spectra are supported by the results in Table 5.4. When comparing polluted background to polluted roadside all metals and metal clusters show elevated levels of particles at the roadside site illustrating a stronger metal source at the roadside. Most of the metals detected will have both natural and anthropogenic sources, such as Fe that has been found to be present in vehicle emissions (Huang 1994), along with observations of increased iron concentrations during studies of Asian dust events (Kim 2003). Iron has also been used in the past as a tracer for industrial activities such as steel manufacturing. (Huang 1994). In this study 1.57% of the particles detected at the clean background site contain iron compared to an increase of 1.99% during more polluted times. This suggests that the polluted air mass has transported additional iron to the site after passing over the highly industrial areas of Northern Germany. Further comparison with the polluted roadside measurements show particulate iron to increase to 5.15% indicating supplementary roadside sources. Other metals that show a similar roadside increment include lithium, copper, potassium and barium. The metal clusters, FeO$_3^-$, SiO$_3^-$ and TiO$^-$, appear to follow a different pattern, with lowest occurrence at the polluted background and highest at the polluted roadside. The common element among all these clusters is that they have all been observed as constituents in soil particles as demonstrated in work by Silva et al. (2000). Other sources do exist for these clusters including road dust and some brake lining samples, therefore it is not surprising to see an increase at the road side presumably due to re-suspension of road dust and soil.
5.5.3.3 Variation of composition with particle size

Due to different formation mechanisms that have been proposed for accumulation mode and coarse mode particles it should not be surprising to find that certain categories of particle appear more frequently in one size category compared to another. For example, previous data collected with the LAMPAS at a remote mountainous site near the German/Czech border has shown that small size ranges were dominated by pure inorganic components and very few small particles were associated with particles containing secondary species (Held et al., 2002). Figure 5.15 illustrates how the composition of 0.7 µm and 2 µm particles varied during this study at both the background and roadside sites. It is worth noting that the composition of the 2 µm particles represents far fewer particles than the 0.7 µm particles, most probably due to a smaller number concentration of coarse particles present in the atmosphere.

Initially it can be seen that the composition of coarse and fine particles recorded at both sites are very different. As described in section 5.5.3.2 this arises as a consequence of a change in air mass from clean to polluted whilst moving from the background to the roadside site. Keeping this in mind, it can be seen that under clean background conditions the sodium- or potassium-only species comprises 36% of the 0.7 µm particles compared to only 6% of the 2 µm particles. This does not mean that the total amount of sodium and potassium containing species has reduced. Rather, it suggests secondary process at work in the evolution of the 2 µm particles, such as the condensation of gases onto the particle surface causing them to grow, and resulting in a decrease of pure Na⁺ or K⁺ particles with increasing diameter. A similar trend is observed at the roadside.
Figure 5.15 Particle composition categories of 0.7 µm and 2 µm particles collected at the background and roadside sites during the London winter sampling campaign.

### a) Background

- **0.7 µm**
  - Aged carbon: 18%
  - Elemental carbon: 24%
  - Mixed Nitrate/Sulphate: 3%
  - Sodium/Potassium only: 11%
  - Nitrate only: 4%
  - Secondary: 36%
  - Sulphate only: 55%
  - Other: 18%

- **2 µm**
  - Aged carbon: 18%
  - Elemental carbon: 9%
  - Mixed Nitrate/Sulphate: 6%
  - Sodium/Potassium only: 9%
  - Nitrate only: 21%
  - Secondary: 43%
  - Sulphate only: 7%
  - Other: 55%

### b) Roadside

- **0.7 µm**
  - Aged carbon: 21%
  - Elemental carbon: 43%
  - Mixed Nitrate/Sulphate: 7%
  - Sodium/Potassium only: 16%
  - Nitrate only: 5%
  - Secondary: 45%
  - Sulphate only: 7%
  - Other: 14%

- **2 µm**
  - Aged carbon: 23%
  - Elemental carbon: 47%
  - Mixed Nitrate/Sulphate: 7%
  - Sodium/Potassium only: 23%
  - Nitrate only: 9%
  - Secondary: 5%
  - Sulphate only: 7%
  - Other: 9%
Another notable feature is that the sulphate-only class only occurs in the 0.7 µm particles and not at all in the 2 µm size. Again this can be explained by the origin of sulphate particles, and their creation and growth into the accumulation mode size range as exemplified by 0.7 µm particles. Sulphate found in the coarse mode, represented by the 2 µm particles is likely to have condensed or agglomerated onto pre-existing coarse particles, therefore making it less likely that a pure coarse sulphate particle will be detected. The observation of secondary processes in the production of coarse particles is reinforced by the increase of ammonium from 1% for the 0.7 µm particles to 7% for the 2 µm particles. This observation does not fit with bulk data results that indicate increased concentrations of ammonium in fine particles. This is clearly seen in the bulk data described in Sections 5.5.2.1 and 5.5.2.2. There are a number of reasons why this is not reflected in the LAMPAS data, the main one being that the fine ammonium-containing particles most probably occur as pure ammonium sulphate particles that are transparent to the nitrogen laser energy. An intriguing feature of this data is the apparent increase in elemental carbon between 0.7 µm and 2 µm particles. This observation contradicts the general belief that carbonaceous particles are more prevalent in the finer particle fraction than the coarse, as well as differing from other data collected in this study. It also contradicts the theory established here that more speciation mixing occurs among coarse particles. No explanation for this observation is available at this time.

For comparison, Figure 5.16 illustrates how the fine and coarse composition at the background site changes under extreme polluted conditions. The polluted background and roadside measurements were both collected when air masses arriving into London had spent a considerable amount of time passing over highly populated inland
regions. It is therefore not surprising to find that similar patterns are seen in both roadside samples (Figure 5.15b) and polluted background samples (Figure 5.16).

**Figure 5.16.** Particle composition of 0.7 \(\mu\)m and 2 \(\mu\)m particles collected at the background during a pollution episode from the London winter sampling campaign.

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5.6 LONDON SUMMER CAMPAIGN RESULTS

5.6.1 Air Mass Back Trajectories

Air mass back trajectories, shown in Figure 5.17, reveal that air masses arriving at the London receptor sites throughout the summer campaign were very consistent, with all trajectories showing air masses that arrived from the west after crossing the Atlantic Ocean, then passing over the south west regions of the UK. Slight differences in the route taken by the trajectories are noted for 26/07/01, in Figures 5.17c, d and e, when air masses arriving at the stated times had previously passed over London.

5.6.2 Bulk Chemical Data and Particle Size Distributions

The techniques and time resolution used for characterising the chemical and physical properties of atmospheric aerosols during the summer London campaign are summarised in Table 5.2. The following sections give account of the results gained from bulk chemical analysis and particle size distributions.
5.6.2.1 Partisol data

Figure 5.18 illustrates the mean aerosol composition at the background and roadside sites. Additional cation analysis, comprising Na\(^+\), K\(^+\), Mg\(^+\) and Ca\(^+\), has been carried out for the summer data that was absent from the winter campaign results. Table 5.5 gives a statistical summary of the Partisol samples. The magnesium and calcium results for the fine aerosol have been omitted due to the majority of samples being below the limit of detection for these species. Comparisons with other major cities show that nitrate and sulphate concentrations measured in this study are generally elevated (Chan et al., 1999; Roosli et al., 2001). Concentrations of other ions such as chloride and sodium are also very variable and depend greatly on the site, for example PM\(_{2.5-10}\) measurements taken in Brisbane, on the east coast of Australia are dominated by Cl\(^-\) and Na\(^+\), whereas for London and Basel these are more minor constituents (Chan et al., 1999; Roosli et al., 2001).

Figure 5.17. 5-day back trajectories for air masses arriving at the London receptor sites during the summer campaign.

a) 1200 hours BST 24/07/01
b) 0000 hours BST 25/07/01

c) 1200 hours BST 25/07/01

d) 0000 hours BST 26/07/01
Figure 5.18. Aerosol mean composition determined for Partisol samples during the London summer campaign.
Table 5.5. The average, minimum, maximum and standard deviation of particulate \( \text{NH}_4^+ \), \( \text{Cl}^- \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{K}^+ \), \( \text{Mg}^+ \) and \( \text{Ca}^+ \) at two sites in London (Summer 2001) compared with PM\(_{10}\) concentrations in other major cities.

<table>
<thead>
<tr>
<th>Site</th>
<th>( \text{NH}_4^+ ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{Cl}^- ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{NO}_3^- ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{SO}_4^{2-} ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{Na}^+ ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{K}^+ ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{Mg}^+ ) (( \mu \text{g m}^{-3} ))</th>
<th>( \text{Ca}^+ ) (( \mu \text{g m}^{-3} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>average</td>
<td>0.10</td>
<td>0.06</td>
<td>1.02</td>
<td>0.29</td>
<td>0.14</td>
<td>0.03</td>
<td>0.05</td>
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<td>Min</td>
<td>0.03</td>
<td>0.03</td>
<td>0.81</td>
<td>0.11</td>
<td>0.10</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
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<td>0.09</td>
<td>1.53</td>
<td>0.63</td>
<td>0.17</td>
<td>0.04</td>
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</tr>
<tr>
<td></td>
<td>sd</td>
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<td>1.01</td>
<td>0.35</td>
<td>0.22</td>
<td>0.51</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>Roadside</td>
<td>average</td>
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<td>0.05</td>
<td>1.21</td>
<td>0.65</td>
<td>0.15</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Min</td>
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<td>0.02</td>
<td>0.66</td>
<td>0.51</td>
<td>0.07</td>
<td>0.00</td>
<td>0.03</td>
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<tr>
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<td>0.02</td>
<td>0.43</td>
<td>0.13</td>
<td>0.05</td>
<td>0.02</td>
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<tr>
<td>Brisbane(^b)</td>
<td>average</td>
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<td>0.45</td>
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<td>0.90</td>
<td>0.90</td>
<td>0.043</td>
<td>0.132</td>
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</tr>
<tr>
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<td>0.36</td>
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<td>0.07</td>
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<tr>
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<td>0.01</td>
<td>0.21</td>
<td>1.70</td>
<td>0.06</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
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<td>0.48</td>
<td>5.37</td>
<td>0.08</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sd</td>
<td>0.41</td>
<td>0.57</td>
<td>0.30</td>
<td>1.26</td>
<td>0.29</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Roadside</td>
<td>average</td>
<td>1.98</td>
<td>0.04</td>
<td>0.42</td>
<td>6.20</td>
<td>0.07</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>1.79</td>
<td>0.02</td>
<td>0.25</td>
<td>5.43</td>
<td>0.05</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>2.19</td>
<td>0.08</td>
<td>0.57</td>
<td>7.01</td>
<td>0.10</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sd</td>
<td>0.17</td>
<td>0.02</td>
<td>0.12</td>
<td>0.63</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Brisbane(^b)</td>
<td>average</td>
<td>0.15</td>
<td>0.18</td>
<td>0.79</td>
<td>0.28</td>
<td>0.28</td>
<td>0.055</td>
<td>0.037</td>
</tr>
<tr>
<td>( \text{PM}_{10})</td>
<td>Background</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>1.18</td>
<td>0.041</td>
<td>1.08</td>
<td>4.10</td>
<td>0.63</td>
<td>0.72</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) = data from Roosli et al., 2001  
\(^b\) = data from Chan et al., 1999

The results obtained from the Partisol data show the following attributes:

- at both roadside and background sites the sulphate and ammonium reside predominantly in the fine fraction. This is consistent with a previous study that found over 85% of sulphate and 95% of ammonium in the fine mode (Zhuang et al., 1999). High concentrations of these species in fine particles are usually indicative of long-range transport over polluted areas. Coarse mode sulphate, found in soil and sea-salt particles, has also been observed peaking around 4 \( \mu \text{m} \) but contributes far less to the overall \( \text{PM}_{10}\) concentration.
• the concentration of potassium is also seen to increase in the fine particle fraction, an observation that was also evident at the Brisbane site. This is presumably indicating that there are at least two potassium sources, the coarse being soil/biogenic derived and the fine due to combustion.

• the nitrate shows a very different trend to that observed during the winter campaign. On this occasion nitrate is found largely in the coarse particle fraction. Research has shown that coarse particulate nitrate is formed in the atmosphere through reactions of nitric acid with coarse sea salt aerosols (Harrison, 1994; Solomon, 1992). Other studies have also provided evidence of coarse nitrate formation by the reaction of nitric acid with soil particles (Pakkanen, 1996; Mamane, 1992).

• other species that dominate the coarse particle fraction include sodium, chloride, magnesium and calcium. The concentrations of all these constituents decrease when moving from the coarse to the fine particles fractions. This observation illustrates the major source of each species including coarse sea salt particles that bring with it high concentrations of sodium and chloride, and to a lesser extent magnesium, whilst the main source of calcium is from re-suspended road dust or soil.

The composition of each individual Partisol sample is given in Appendix III.

5.6.2.2 Impactor data

Similar trends between coarse and fine components that were illustrated by the Partisol results were also seen with the MOUDI data. An example of some of the
MOUDI data obtained is given in Section 5.6.3.5 that compares single particle data with bulk data.

5.6.2.3 Particle size distributions and gas data

Figure 5.19 displays size distributions measured with the Scanning Mobility Particle Sizer. The data has been analysed according to the time interval measured with the Partisol, therefore each distribution represents a four hour average and is denoted by the midpoint of each measuring period. The particle size distributions from the Regent’s Park background site, Figure 5.19a, show a large temporal variation in the modal diameter. Throughout 24/07/01 the modal diameter is generally around 40 nm indicating that local traffic sources are influencing the site. The modal diameter changes dramatically during 25/07/01 to approximately 100 nm, showing that the aerosols are more substantially coagulated. This demonstrates that the site is now under the influence of long-range transported aerosol rather than local traffic sources.

The evaluation of the size distributions at Exhibition Road, Figure 5.19b, shows that number concentration are generally slightly higher at the roadside site. In the main, there are two modal diameters prevalent, the finest mode occurs around 30-40 nm, similar to the mode observed during the winter campaign. The second mode is found around 100 nm and is very similar to the mode found at the background site during 25/07/01. These two modes indicate that the roadside site is influenced by local traffic and long-range sources. This is confirmed by comparing size distribution collected during peak hours (e.g. 26/07/01; 07:00) to those collected at off-peak times (e.g. 26/07/01; 03:00).
Figure 5.20 illustrates data from combined SMPS and APS measurements. These show that almost continuous particles size distributions can be obtained by using both these instruments simultaneously. They also demonstrate well how the modal diameter increases when changing from number concentration to surface area. Figure 5.21 shows how these surface area distributions can be used to reflect changing atmospheric conditions.

5.6.2.4 Carbon analyser

Average concentrations for elemental and organic carbon have been incorporated into the overall PM$_{10}$ composition, as shown in Figure 5.22. It is seen that elemental carbon is a major constituent of PM$_{10}$ at both the background and roadside sites. Comparing between the two sites it can be seen that the concentrations of both carbon species are higher at the roadside site, with the increase in elemental carbon being far more pronounced. This is no surprise as particulate elemental carbon is associated with primary combustion sources. This is verified by Figure 5.23, showing the correlation of NO$_x$ versus elemental carbon and organic carbon. In comparison, organic carbon has primary and secondary sources. Primary organic carbon can be produced directly from combustion engines or from mechanical sources such as tyre wear or emission of pollen spores or soil particles. Secondary sources include gas to particle conversion of volatile organic compounds via condensation of chemical adsorption. Past studies have shown that secondary organic carbon concentrations are significantly higher during the summer when photochemical activity is favoured (Castro et al., 1999).
Figure 5.19. Particle size distribution data determined from SMPS measurements during the London summer 2001 campaign.

Figure 5.20. Particle size distribution data from SMPS (grey) and APS (red) during the London summer campaign.

a) Background number concentration

b) Background surface area concentration

c) Roadside number concentration

c) Roadside surface area concentration
Figure 5.21. Calculated particle surface area (colour) as a function of log particle diameter and time of sampling, July 2001.
Figure 5.22. Average aerosol composition of PM$_{10}$ at two London sites from the Partisol and carbon analyser data during the summer campaign.

![Aerosol Composition](image)

5.6.3 Single Particle Data

5.6.3.1 LAMPAS count rate

Figure 5.24 illustrates the 24-hour measuring period that took place at the Regent’s Park background site. Sampling with the LAMPAS ran from 12:30 BST on 24/07/01 until 12:30 BST on 25/07/01. During this time 13,453 particles were detected, giving

\[
y = 0.0636x + 0.9629 \\
R^2 = 0.3184
\]

\[
y = 0.0189x + 0.9316 \\
R^2 = 0.2303
\]
an average detection rate of 12 counts per minute. This count rate is a dramatic increase from rates recorded during the PUMA and winter London campaigns. The main reason for this increase is due to the new excimer laser that replaced the nitrogen laser which was present during previous measurement campaigns.

Figure 5.24. The PM$_{2.5}$ ion concentration and the LAMPAS count rate for the period ending at 1230 hours BST on 25/07/01.

The analogous roadside measurements are depicted in Figure 5.25. Measuring at this site took place from 2300 hours BST on 25/07/01 until 17:30 hours BST on 26/07/01.
Again, particle count rates remained high with over 12,000 particles detected, an average detection rate of 14 counts per minute.

Figure 5.25. The PM$_{2.5}$ ion concentration and the LAMPAS count rate for the period ending 1700 hours BST on 26/07/01.

5.6.3.2 **Excimer laser and hourly averages**

Due to the replacement of the nitrogen laser with an excimer laser, it is appropriate to investigate any changes in the ionisation/desorption process that may produce differences in the ions detected. Using the hourly averages in Figure 5.26 it can be
seen that some similar peak combinations arise in both the positive and negative spectra that were observed with the nitrogen laser, such as the positive peaks, Na\(^+\), NH\(_4\)\(^+\), Al\(^+\), K\(^+\) and the negative peaks, CN\(^-\)/CNO\(^-\), Cl\(^-\), NO\(_2\)\(^-\), NO\(_3\)\(^-\), HSO\(_4\)\(^-\) and the negative carbon series.

Figure 5.26 Examples of hourly averaged spectra for particles collected at a) the background site and b) the roadside site using an excimer laser for the ionisation/desorption process.

a) Background site from 24/07/01 till 25/07/01

i) 1800-1900 BST

ii) 2000-0300 BST

iii) 0600-0700 BST
b) Roadside site from 25/07/01 until 26/07/01

i) 0200-0300 BST

ii) 0800-0900 BST

iii) 1600-1700 BST
Figure 5.26 also gives evidence of additional ions being formed with the excimer laser that were not observed with the nitrogen laser. In particular, the positive spectrum in Figure 5.26 a(i) depicts intense peaks at \( m/z = 41, 55, 67, 81 \) and 91. It is very difficult to ascertain what these peaks are just by using the average spectra, but when the individual spectral patterns containing these peaks are investigated a great deal can be learnt about their origins. Figure 5.27 gives examples of individual spectra that contain the unknown mass to charge ratios. These show that it is a common occurrence to observe \( m/z = 41, 55, 67 \) and 91 in the same spectral pattern implying that these peaks are somehow related. They also usually occur with other smaller peaks such as \( m/z = 43 \) or 57 creating clusters around each major peak. The analogous characteristics of the negative spectrum include the presence of \( \text{CN}^- \), \( \text{NO}_2^- \), \( C_n^- \) series and \( \text{OH}^- \), illustrating that carbon is a major component of these particles. Therefore the unknown peaks, and their surrounding clusters, may well represent a range of carbon fragmentation patterns, as exemplified in Table 5.6. Another feature that became apparent by manually inspecting individual spectra was that \( m/z = 27 \) may also represent carbon fragmentation as it is often seen with a strong peak at \( m/z = 29 \), as in Figure 5.27c. In comparison, Figure 5.27d illustrates peaks at \( m/z = 27, 39 \) that represent the metal ions \( \text{Al}^+ \) and \( \text{K}^+ \). These are confirmed by the presence of other metal constituents at \( m/z = 7, 23 \) and 56 that reveal lithium, sodium and iron occurring. The negative spectrum is also very different to the others observed due to the presence of a dominant nitrite peak, along with peaks at \( m/z = -35, -59, -73, -76 \) and -88 showing \( \text{Cl}^- \), \( \text{C}_2\text{H}_3\text{O}^- \), \( \text{C}_3\text{H}_5\text{O}^- \), \( \text{SiO}_3^- \) and \( \text{FeO}_2^- \). The spectral patterns in
Figure 5.27a-c compared to those in Figure 5.27d, provide evidence that two very different sources are contributing.

Figure 5.27. Examples of individual spectral patterns analysed at the background site 1800-1900 hours BST.

Table 5.6 Possible fragmentation patterns for the unknown positive ions produced by ionisation/desorption using an excimer laser.

<table>
<thead>
<tr>
<th>M/Z</th>
<th>Fragmentation ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>CH+</td>
</tr>
<tr>
<td>15</td>
<td>CH$_3$+</td>
</tr>
<tr>
<td>27</td>
<td>??</td>
</tr>
<tr>
<td>29</td>
<td>??</td>
</tr>
<tr>
<td>41</td>
<td>C$_2$HO+</td>
</tr>
<tr>
<td>43</td>
<td>C$_2$H$_3$O+</td>
</tr>
<tr>
<td>55</td>
<td>C$_3$H$_3$O+</td>
</tr>
<tr>
<td>57</td>
<td>C$_3$H$_2$O+</td>
</tr>
<tr>
<td>67</td>
<td>??</td>
</tr>
<tr>
<td>69</td>
<td>C$_3$HO$_2$+</td>
</tr>
<tr>
<td>81</td>
<td>C$_4$HO$_2$+</td>
</tr>
<tr>
<td>91</td>
<td>C$_5$H$_3$O$_2$+</td>
</tr>
</tbody>
</table>

In terms of the overall spectral patterns that are seen, the hourly averages indicate that from time to time dramatic changes in overall particle composition did take place.
This is exemplified strongly by two occasions. The first took place between 0400 hours and 0500 hours BST on 25/07/01, at the background site. Changes were observed in the negative spectra by the increasing intensity of the nitrate peak at m/z = -62, as revealed in Figure 5.2.7a(iii); previous spectra had not contained dominant nitrate peaks, only a fairly strong nitrite peak at m/z = -46, which in itself is an unusual occurrence when compared to the NO₂⁻/NO₃⁻ combination typically observed with the nitrogen laser. The occurrence of the nitrate peak was accompanied by a reduction in CN⁻ and CNO⁻ peaks, observed in Figures 5.27a(i)(ii), as well as a decrease in the observation of Cₙ⁻ peaks. Interestingly, this compositional change correlates with a corresponding increase in concentration of sulphate and ammonium in the PM₂.₅ fraction, as shown in Figure 5.24. Changes observed in the positive spectral patterns include the development of peaks at m/z = 18, 30, 44 and 58. The individual spectra in Figure 5.28 reveal the typical spectra these peaks occur in.

![Figure 5.28 Examples of individual particle composition collected between 0700 hours and 0800 hours BST 25/07/01 at the background site.](image)

These patterns were initially observed around 0400 hours BST 25/07/01, and continued to be a feature throughout the rest of the monitoring period at Regent’s Park.
The second obvious change in overall particle composition occurred between 1200 hours and 1300 hours BST 26/07/01 at the Exhibition Road site. This is exemplified by comparing the hourly averages in Figures 5.27b(ii) and (iii). These show that the nitrite and nitrate peaks that were clearly the dominant feature of the negative spectra observed during period the previous 24 hours have been replaced by an increase in carbon-containing spectra as indicated by the stronger CN⁻/CNO⁻ peaks at m/z = -26/-42 in Figure 5.27b(ii), showing that the spectra collected after 1200 hours have very similar qualities as those observed before the first pattern change at the Regent’s Park site, given in Figures 5.27a(i) and (ii).

5.6.3.3 ATOFMS count rate

Overlapping single particle measurements were made with the TSI Model 3600 Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) from 0700 hours BST until 1700 hours BST on 26/07/01, whilst at the roadside site. During this time 1625 particles were detected and analysed by the ATOFMS giving an average count rate of 4 counts per minute. This count rate is much smaller than observed with the LAMPAS due to the larger diameter of the excimer beam compared to the Nd:Yag laser in the ATOFMS.

Figure 5.29 The size-segregated count rate of particles analysed with the ATOFMS during the summer London campaign.
Figure 5.29 illustrates the count rate of the analysed particles during the monitoring period, given in counts per hour so the variation in count rate between particle size ranges can be clearly seen. This figure illustrates that the majority of particles analysed are between 1 µm and 2.5 µm in diameter, with much smaller count rates being seen for the PM$_{0.5}$ and PM$_{>2.5}$ particle fractions.

5.6.3.4 **ATOFMS size distributions**

Individual size distributions gained during this campaign will not be considered here as APS and SMPS data covers this topic. Examples of the size distributions that can be obtained with the ATOFMS are presented in Section 6.

5.6.3.5 **Nd:Yag laser and hourly averages**

Since monitoring at the roadside site took place simultaneously with the LAMPAS and ATOFMS a direct comparison could be made between the two single particle techniques. The main difference between the two instruments lies in the desorption/ionisation process of the particles. The ATOFMS employs a Nd:Yag laser fourth harmonic at 266 nm, and the LAMPAS an excimer 198 nm.

Figure 5.31 illustrates hourly averages obtained with the ATOFMS that were measured during comparable times to the LAMPAS hourly averages in Figure 5.27b(ii) and (iii). Typical peaks that are seen with the Nd:Yag laser include m/z = 12, 23, 27, 36, 56 and 63 that represent the positive peaks C$_1^+$, Na$^+$, Al$^+$, C$_3^+$, Fe$^+$ and Cu$^+$. Negative peaks that are regularly observed include m/z = -16/-17, -26, -35, -42, -46/-62, -79, -80, -96/-97 and -125 giving evidence of the species O’/OH’, CN’, Cl’,
CNO\(^{-}\), NO\(_2^-\)/NO\(_3^-\), PO\(_3^-\), SO\(_3^-\), SO\(_4^-\)/HSO\(_4^-\) and HNO\(_3^-\)/NO\(_3^-\). Some similar negative peaks were also observed with the excimer laser, but the real difference is seen when the combinations of these peaks are inspected. For example, the ATOFMS data showed that CN\(^-\) and CNO\(^-\) occurred among many different spectral patterns, as shown in Figure 5.32a-c, whereas when they occurred in the LAMPAS excimer data the spectral patterns were very uniform, usually being combined with HSO\(_4^-\), NO\(_2^-\) and carbon components (Figure 5.27). The LAMPAS results also suggest that it is rare to view phosphate, PO\(_3^-\) among the spectra peaks, whereas PO\(_3^-\) was often observed among the ATOFMS data, as given by the example spectrum in Figure 5.32a. This could have important implications in source apportionment as PO\(_3^-\) has been used in the past for source apportionment of biogenic particles and could be used for future, in combination with other peaks, to apportion sources such as particles released from steel work sintering processes, as suggested from fingerprinting results.

Different spectral patterns are also evident for carbon containing particles, for example strong C\(_n^-\) chains are often observed in the ATOFMS data that are usually representative of diesel emitted particles as given in Figure 5.32d. These carbon patterns are not seen as regularly among the LAMPAS excimer spectra, instead carbon patterns in the form of peaks at 41/43 and 67/69 etc are seen. As yet the identity of such peaks has not been clarified, although it seems reasonable to expect that more laboratory work with the excimer laser will lead to the establishment of a different set of fingerprints for diesel sources.

Figure 5.32 goes some way in illustrating the different metal species that can be detected with the Nd:Yag laser in the ATOFMS. As well as the regular metal species, sodium and potassium found at m/z = 23 and 39, other metals, such as calcium (m/z =
iron and iron oxide (m/z = 56/-88), aluminium (m/z = 27), copper (m/z = 63), barium and barium oxide (m/z = 138/154) have all been noted. Such metal constituents are also very important tools for source apportionment as proven by the fingerprinting undertaken in this work. As yet it has not been established whether similar metals can be detected easily with the excimer laser, but the fieldwork here suggests that the excimer is not as sensitive as the Nd:Yag laser to such metals.

Figure 5.31. Examples of hourly averaged spectra for particles collected at the roadside site using an Nd:Yag laser for the ionisation/desorption process.

a) 0800 to 0900 hours BST on 26/07/01

b) 1600 to 1700 hours BST on 26/07/01
5.6.3.6 Single particle versus bulk techniques

So far single particle analysis has been employed to distinguish between individual particles and to identify sources that influence the production of different particle types. Another aim of this project was to compare data results obtained via single particle analysis and bulk filter analysis. In the past, attempts to reconcile single particle measurements with bulk quantitative measurements have been made by applying relative sensitivity factors to certain components, but so far results have shown at best only semi-quantitative agreement (Mansorri et al., 1994; Gross et al., 2000b; Mansoori et al, 1994). Despite these limitations, an attempt to evaluate how quantitative single particle analysis can be, was made. To compare directly single particle techniques to bulk filter methods a number of procedures have to be carried...
out so that the results presented have maximum comparability. These steps are outlined below:

(1) Both single particle instruments deliver a lot more chemical information than the bulk techniques, therefore prior to comparison, the atmospheric constituents that are going to be compared must be filtered from the remaining spectral peaks. The search criteria used are given in Table 5.7 and were chosen based on the previous analysis. In some cases, interference caused by other ion species may arise, for example a strong potassium peak at m/z = 39 may cause ringing that may lead to the number of calcium peaks being overestimated. For this reason the peaks at m/z = 40 that followed a very intense potassium peak had to be disregarded. Each peak that satisfied the criteria in Table 5.7 contributed 1 unit to that species.

<table>
<thead>
<tr>
<th>Species</th>
<th>M/Z</th>
<th>LAMPAS</th>
<th>ATOFMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>-46</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td></td>
<td>-62</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>Sulphate</td>
<td>-80</td>
<td>♦</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-97</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>-35</td>
<td>♦</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(2) Due to single particle and bulk filter techniques having very different time resolutions the SPMS peaks selected must be grouped and summed according to the corresponding time period of the filter sample.

(3) In step 1, no stipulations were enforced for peak height or area. Instead, each component has been weighted according to the diameter, $D_p$, of particle it was detected in. This meant each unit was multiplied by $[(Dp)^3]/6$. If unit density is assumed, this value can now be converted into a mass ($\mu g$). This type of factorisation procedure can only be applied to the ATOFMS data as the active triggering on this instrument allows for simultaneous particle sizing and composition. Exact particle size information was not available for the LAMPAS data, the only information provided was that the particles detected were within the size range $0.3\,\mu m < D_p < 1.2\,\mu m$. For this reason all LAMPAS data were weighted using the midpoint of the size range, $D_p = 0.9\,\mu m$.

(4) Next a correction was applied to the number concentration using the formula:

$$Y = 0.0026 \, (Dp)^{4.4007}$$

This is a function which corrects for inlet efficiency.

(5) Results in this study and other work have established that the ionisation/desorption process is more sensitive to some constituents than for others, as exemplified by intense sodium and potassium signals in both the LAMPAS and ATOFMS data. Therefore, application of relative sensitivity
factors (RSF) for each species is required as listed in Table 5.8. Most of the
RSF values given here have been established via work carried out within our
research laboratories using equi-molar solutions of known composition. At
present these factors are tentative and further work is required to confirm such
values.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>RSF</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/Na</td>
<td>5*</td>
</tr>
<tr>
<td>NH4/Na</td>
<td>0.014*</td>
</tr>
<tr>
<td>Ca/Na</td>
<td>0.12</td>
</tr>
<tr>
<td>SO4/NO3</td>
<td>0.57</td>
</tr>
<tr>
<td>Cl/NO3</td>
<td>0.51</td>
</tr>
<tr>
<td>Na/NO3</td>
<td>3</td>
</tr>
<tr>
<td>K/NO3</td>
<td>15</td>
</tr>
<tr>
<td>NH4/NO3</td>
<td>0.042</td>
</tr>
<tr>
<td>Ca/NO3</td>
<td>0.36</td>
</tr>
</tbody>
</table>

* = Literature value [7]

(6) Finally, each species is normalised for the total volume sampled so that the
results have the units µg m⁻³.

The results gained after following this procedure are given separately for each single
particle technique:

(a) Linear correlation of LAMPAS versus Partisol

The LAMPAS results have been compared with the fine fraction sampled with the
Partisol. It should be noted that the two techniques do not measure the same particle
size range. Figure 5.33 illustrates the overlap of size ranges between the two
methods, with the LAMPAS only being able to detect a small fraction of the total
particulate concentration measured by the fine Partisol fraction. This discrepancy must be taken into account when comparing results between both methods.

Figure 5.33. Illustration of size ranges detected by the LAMPAS and Partisol.

The following graph (Figure 5.34) shows how well the concentrations of each species as measured by the two techniques correlate. The y-axis has been labelled relative LAMPAS mass concentration as the exact particle size is unknown and therefore precise mass concentrations cannot be derived. This is primarily due to the large spot size of the ionisation/desorption excimer laser that leads to an extension of the particle size range for any single size setting. The size range measured is determined by calibrating the laser detection-ionisation set-up using latex spheres of a known diameter. On this occasion the calibration was within the size range 0.3 µm <Dp<1.2µm that encompassed 75% of the particles detected, with the modal Dp occurring at the midpoint, Dp = 0.9 µm. The modal diameter was used in the calculation described previously.
Figure 5.34 depicts linear regression plots for each individual species. None of plots shows a one to one relationship. Instead, the LAMPAS severely underestimates the relative mass concentrations. This can most probably be explained by the lower
detection efficiency of the LAMPAS due to the particle losses that occur at the inlet. Field measurements comparing number concentrations measured by the LAMPAS and APS have derived an initial LAMPAS detection efficiency of $2.5 \times 10^{-4}$ as illustrated in Figure 5.35. This detection efficiency represents the regression slope of number of particles detected by the LAMPAS to the number detected by the APS in the same time period. The value gained here is in good agreement with literature values of $10^{-5} – 10^{-3}$ for particles in the size range 200nm – 800nm, respectively (Hinz et al., 1994).

**Figure 5.35. Detection efficiency of LAMPAS derived by co-located field measurements.**

If a closer look is taken at the regression results in Figure 5.34 it can be seen that there is a reasonable correlation between methods for the detection of potassium and nitrate species. At present there is little known about the sources of potassium, but MOUDI and Partisol results obtained here show that it is found in both the fine and coarse particle size fractions but only in small concentrations ($0.03 – 0.1 \ \mu g \ m^{-3}$). The MOUDI results shown in Figure 5.36 indicate that it is most prevalent on stages 4 and 8, corresponding to particles in the ranges $2 – 10 \ \mu m$ and $0.2 – 1 \ \mu m$ respectively.
The fact that potassium correlates so well between the two methods could be due to the LAMPAS measuring nearly the exact size range in which potassium falls. This argument is reinforced on consideration of the low $R^2$ value for the sodium species. If the relative MOUDI distributions are considered (Figure 5.36) it can be seen that stage 8 does not have the greatest loadings, instead these are found on stages 4 and 5 (ie. in more coarse particles). It is therefore not surprising to find sodium with the lowest $R^2$ value. The remaining correlations also show low $R^2$ values for ammonium and sulphate. This time ammonium and sulphate species have the largest loadings on stage 8 but also have additional smaller loadings on stage 5 and the after filter. These extra loadings will be detected by the Partisol but not by the LAMPAS because of the incompatible size ranges. An exception to this theory is nitrate that correlates well between both techniques even though there is a high loading on stage 5. This indicates that there are other factors at work here including the lower response of the instrument for ammonium and sulphate.

**Figure 5.36.** Average MOUDI loadings during July, 2001 London campaign.

Comparison between calcium for these two techniques was not possible as very little calcium was detected on the fine filters and it is very difficult to depict a true $Ca^+$ peak as this signal is not very intense and there is possible interference from strong potassium peaks.
The pie-charts shown in Figure 5.37 compare 4-hourly Partisol and LAMPAS composition measurements. These plots do not show good agreement and are a good demonstration of why inlet correction factors and relative sensitivity factors for each species are required.

As yet no relative sensitivity factors have been reported for the LAMPAS technique. To be able to address this dilemma research must be undertaken to provide such factors. To some extent relative sensitivity factors have been developed in the present work by the linear regression of bulk methods versus the LAMPAS. The following section will illustrate how RSFs can be applied to the SPMS technique by using values derived from the ATOFMS.

(b) Application of relative sensitivity factors with ATOFMS data

Figure 5.38 illustrates particle composition as monitored by the ATOFMS. The uncorrected pie-chart shows the data without applying any RSF values. The corrected pie-chart demonstrates what effect each RSF has, as given in Table 5.8, on the relative magnitude of each species.

If the uncorrected plot illustrated in Figure 5.39 is compared with the Partisol data obtained during the same time period (Figure 5.39) then it comes as no surprise to observe that the proportions of potassium and sodium concentrations are being grossly overestimated by the ATOFMS, whilst the ammonium is being underestimated. These observations are well known and have been characterised both in this work and in the literature. What is more surprising is the large difference in the proportion of sulphate that is being monitored. These results show that the ATOFMS is less
sensitive to sulphate than the bulk method. The corrected plot in Figure 5.38 shows a slight improvement in the proportions of species but still there are major differences seen when comparing with the Partisol results.

One point to note when comparing these two sets of data is that the size ranges between the two techniques being considered differ. This is due to the inlet design of the ATOFMS, which causes the detection efficiency to reduce abruptly above 3 µm diameter. Therefore particles > 3 µm will not be measured using the ATOFMS technique but will be accounted for by the Partisol. Unfortunately, this problem cannot be resolved by merely using the fine fraction as again the ATOFMS has reduced detection efficiency below 0.3 µm. To remove any uncertainty surrounding the overlapping size range a direct comparison should be made with the stage 5 MOUDI loadings (1 < Dp (µm) < 2) and the ATOFMS. The results of this comparison are exemplified in Figure 5.40.

These results show that there are still large discrepancies between the relative proportions of ammonium being detected by each method. If ammonium is not included in the total composition as shown in Figure 5.41 it can be seem more clearly that the ATOFMS is also overestimating the proportions of calcium and chloride but is still underestimating the sulphate, though good agreement has been found between nitrate, potassium and sodium.

The results gained so far illustrate how RSFs can be used to help reconcile discrepancies that have been observed between bulk and SPMS techniques. With the improvement of RSFs it is hoped that the discordance that still remains between
species will be reconciled somewhat. A step towards this reconciliation could be found by applying field generated RSFs. The ensuing section illustrates how field generated RSFs may be applied in this work.

(c) Application of field generated RSFs

Co-located ATOFMS and MOUDI field measurements that were recorded at the Regent’s Park background site where used to generate relative sensitivity factors for the ATOFMS, shown in Table 5.9. The following calculation was used to determine each RSF:

\[ \text{Factor} = \frac{[X]_{\text{MOUDI}}}{[X]_{\text{ATOFMS}}} \]

Table 5.9. Field generated RSF values.

<table>
<thead>
<tr>
<th>Species</th>
<th>Stage 8 Factor</th>
<th>Stage 5 Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>8.56</td>
<td>0.0085</td>
</tr>
<tr>
<td>Nitrate</td>
<td>3.40</td>
<td>0.0066</td>
</tr>
<tr>
<td>Sulphate</td>
<td>99.7</td>
<td>0.0162</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.26</td>
<td>0.0004</td>
</tr>
<tr>
<td>Ammonium</td>
<td>159.8</td>
<td>0.0027</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.35</td>
<td>0.0001</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.033</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

The stage 5 RSF values from Table 5.9 were applied to the Imperial College data that has been used in previous examples. The results are shown in Figure 5.42.

Figure 5.42 indicates a number of improvements in the relative proportions of the species. The most obvious is the better agreement of sulphate and the reduction of ammonium as measured by the ATOFMS. A persistent inconsistency between these two methods is proportion of chloride being detected. More field comparison work is needed to help resolve this and other intercomparison issues. It is hoped that with the provision of better field generated RSFs that more insight into these problems will be revealed.
The results so far have shown how SPMS data can be compared to bulk analytical methods. The data manipulation method has demonstrated how two different factors; an inlet correction factor and a relative sensitivity factor can be applied to raw SPMS data so to improve inconsistencies between the two methods. The results discussed also indicate that there may be more factors that need to be included before SPMS can be employed in the same manner as standard bulk methods.
Figure 5.37. Direct comparison of particle composition measured with the Partisol and LAMPAS.

LAMPAS Particle Composition
24/7/01 16:00 - 20:00

Nitrate µg m\(^{-3}\)
0.01

Sulphate µg m\(^{-3}\)
0.03

Chloride µg m\(^{-3}\)
0.01

Partisol Fine Particle Composition
7/24/01 16:00 - 20:00

Nitrate µg m\(^{-3}\)
0.01

Sulphate µg m\(^{-3}\)
0.06

Chloride µg m\(^{-3}\)
0.21

Partisol Fine Particle Composition
7/25/01 04:00 - 08:00

Nitrate µg m\(^{-3}\)
0.01

Sulphate µg m\(^{-3}\)
0.10

Chloride µg m\(^{-3}\)
0.48

Partisol Fine Particle Composition
7/25/01 04:00 - 08:00

Nitrate µg m\(^{-3}\)
0.08

Sulphate µg m\(^{-3}\)
4.54
Figure 5.38. Particle composition before and after the application of relative sensitivity factors.
Figure 5.39. Coarse particle composition as measured by the Partisol.
Figure 5.40. Comparison of MOUDI and ATOFMS data measured at Imperial College using RSF values from Table 5.8.
Figure 5.41. Comparison between MOUDI and ATOFMS particle composition with ammonium removed.

Corrected 1 - 2 um ATOFMS Particle Composition
26/7/01 09:00 - 13:00

1 - 2 um MOUDI Particle Composition
26/7/01 09:00 - 13:00

[Pie charts showing particle composition with ammonium removed]

- Nitrate µg m⁻³
- Sulphate µg m⁻³
- Chloride µg m⁻³
- Ammonium µg m⁻³
- Sodium µg m⁻³
- Potassium µg m⁻³
- Carbon µg m⁻³
- Calcium µg m⁻³
Figure 5.42. The effect of using field data-generated RSFs when applied to the results collected at Imperial College.
6. BIRMINGHAM 2002 CAMPAIGN

6.1 INTRODUCTION

During June and July 2002 the ATOFMS was employed in a long field measurement campaign in Birmingham. Three sites were chosen, each of which had differing degrees of traffic influence:

- Winterbourne, an urban background site;
- Bristol Road, a major A road that runs from southwest to northeast Birmingham;
- Queensway Tunnel, part of the tunnel network that takes traffic through central Birmingham towards the M6 motorway.

The aim of this work was to compare the composition of particles collected at each of these three contrasting sites in Birmingham and to assess the application of the ATOFMS in source apportionment.

6.2 DATA COLLECTION

At each site, the ATOFMS was co-located with a Lasair particle counter and a Hi-Volume sampler. The ATOFMS and Lasair were both housed in a van throughout each measurement period, whilst the Hi-Vol was positioned close to the van. Stainless steel sampling lines were attached to each of the instrument inlets and both were passed through the driver’s window. The length of the sampling lines was less than 3 metres and the amount of bends in each were kept to a minimum. The intricacies of set up at each site are described in the sections below.
6.2.1 Winterbourne

Winterbourne is a site owned by the University of Birmingham as part of the University Botanical Gardens. For this campaign it was used as an urban background site, with sampling taking place approximately 200 metres away from the nearest road. The van was parked in close proximity to greenhouses and other storage houses. Figure 6.1a shows the van and the surrounding area. Sampling started on 25\textsuperscript{th} June and continued for 4 days non-stop. Data was collected in 4 hourly batch samples so make data analysis more efficient.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_1.png}
\caption{Photographs of each sampling site used in the Birmingham 2002 campaign.}
\end{figure}

(a) Background Site – Winterbourne

(b) Roadside Site – Bristol Road
6.2.2 Queensway Tunnel

In this study the Queensway Tunnel site was used to study the road traffic signature. The tunnel is approximately 0.5 km long with the northbound and southbound lanes separated into two by a wall, with occasional gaps. The van was situated about a third of the way down, on the south bound side of the tunnel in a small-lay by usually used by maintenance workers. The photograph in Figure 6.1c illustrates the environment in which the study took place. Due to the air being heavily concentrated with traffic fumes it was only possible to run experiments for a continuous 15 hour period. This set of measurements took place from 0500 hours BST on 02/07/02 until 2000 hours BST on 02/07/02. As a result of the decreased monitoring period, spectra were collected in 1 hour batch intervals. To assist with data analysis variations traffic flow were counted on the hour for 15-minute periods. The plot in Figure 6.2 shows the trend in traffic flows throughout the 15 hours.
The above graph illustrates a slight diurnal trend in the number of cars passing through the tunnel, peaking around 0730 hours BST in the morning and 1630 hours BST in the afternoon. It is expected that a high percentage of the cars have petrol engines, whereas the majority of vans, trucks and buses will be diesel.

6.2.3 **Bristol Road**

In this study the Bristol Road was used as a roadside site. Figure 6.1b shows the exact location that measuring took place with the van parked on the University grounds, next to the south gate entrance. The sampling inlets were positioned approximately 5 metres off the ground, overhanging a wall next to the footpath. Four continual days of sampling began on 06/07/02. As for the Winterbourne measurements single particle data was collected in 4 hourly sample batches.
To assist with data analysis traffic counts were made during the first 24 hour period. These counts were then calibrated against ASTRID, an automatic traffic logger. Figure 6.3 shows the correlations between ASTRID and the manually determined vehicle counts for this period. The variation in traffic flow during the four day measurement period can also be seen in Figure 6.3. A large diurnal variation in traffic flow is seen with over 2000 vehicles passing the receptor site at peak times.

Figure 6.3. Relationship between manual vehicle counts and ASTRID for a) outbound lane sensor No. e.1210:p1 b) inbound lane sensor No. e.1210:qi and c) the variation in traffic flow along the Bristol Road between 8 and 12 of July, 2002.
6.3 DATA ANALYSIS

The single particle data was analysed using MS-Analyse, a software package that has been specifically developed by TSI to inspect and classify each spectrum. The bulk data was analysed using ICP-MS.

6.4 PARTICLE COMPOSITION AT WINTERBOURNE

Using a modified high volume sampler, large size-segregated samples of particulate matter were collected for metal analysis. Bulk sampling periods varied according to changing weather and atmospheric conditions, such that sampling times ranged from 8 to 24 hours. The average concentration for the metals Mg, Al, Ca, Ti, Mn, Fe, Cu, Zn, Ba, Pt, Hg and Pb across the five size ranges that were collected at the Winterbourne site appear in Figure 6.4. Figure 6.5 shows that the elements Mg, Al, Ca and Fe were found distributed throughout nearly all size ranges. High concentrations of these species were detected among the coarser particle fractions in the range $7.2 \, \mu m > D_p > 1.5 \, \mu m$, with aluminium and calcium showing a more bimodal distribution. Smaller quantities of Mn, Cu, Zn, Ba and Pb were also found.
distributed across all particle sizes. The elements that showed a marked increase in the fine fraction included Mn, Cu, Zn and Pb.

In comparison with the bulk data, Figure 6.6a illustrates a typical particle size distribution of particles detected with the ATOFMS at Winterbourne. This diagram compares the number of particles hit and missed during a four-hour measuring period, indicating that approximately 18% of particles detected were hit and consequently analysed. The average composition of particles analysed during this time period is given in Figure 6.6b.
Figure 6.4. The average airborne trace element concentration at the Winterbourne receptor site, according to particle size fraction.
Figure 6.5. Average elemental size distributions at three sites in Birmingham.

(a) Winterbourne

(b) Tunnel

(c) Bristol Road

Legend:
- 3 \mu m < Dp < 7.2 \mu m
- 0.95 \mu m < Dp < 1.5 \mu m
- Dp < 0.5 \mu m
- 1.5 \mu m < Dp < 3 \mu m
- 0.5 \mu m < Dp < 0.95 \mu m
Figure 6.6. Particle count data obtained by the ATOFMS between 0900 hours BST 25/06/02 and 1200 hours BST 25/06/02 showing, (a) particle size distribution of particles detected and (b) average composition of “hit” particles.
The most notable feature of the average particle composition in Figure 6.6b is the dominance of sodium and chloride and their clusters indicated by the peaks at m/z = 23, 46, 63, 81/83, -35/-37 and –93/-95/-97 that represent Na\(^+\), Na\(_2\)\(^+\), Na\(_2\)OH\(^+\), Na\(_2\)\(^{35}\)Cl/Na\(_2\)\(^{37}\)Cl, \(^{35}\)Cl/\(^{37}\)Cl and Na\(^{35}\)Cl\(_2/Na^{37}\)Cl\(_2/Na^{35}\)Cl\(^{37}\)Cl, respectively. These peaks together with the presence of the nitrogen-containing species at m/z = -46 and –62, illustrates that the air mass arriving at the Winterbourne contains an abundance of aged sea-salt aerosols. The bulk metal data and the single particle data presented here both illustrate the presence of magnesium, calcium and iron that can all indicate the presence of crustal sources; Mg is also present in marine aerosol.

6.5 PARTICLE COMPOSITION AT THE QUEENSWAY TUNNEL

Figure 6.7 presents the average trace element composition at the Queensway Tunnel site. It should be noted that the concentration of the analysed species collected at this location are approximately a factor of 100 times greater than those obtained at the Winterbourne site. There was an increase in the number of metals above detection limit at the tunnel site compared to the background Winterbourne site including, Mg, Al, Ca, Mn, Fe, Cu, Zn, Ba and Pb. Nearly all metals were observed throughout the size ranges, with only Pb being absent from the < 0.5 µm size range. Using the average concentrations that can be seen more clearly in Figure 6.5b, it can be seen that almost all these metals have a modal peak occurring in the coarse particle range, in the 1.5 µm < Dp < 3 µm fraction. The fact that these elements occur in the coarse fraction suggests that there are mechanical sources for each metal that most probably relate to the wear of vehicle components. The elements Mg, Al, Ca and Cu all show bimodal distributions indicating that there are other sources contributing to their
overall atmospheric concentration. Zinc displays a very different pattern with a strong modal peak occurring only in the fine fraction, < 0.5 µm.

Figure 6.8a displays a typical particle size distribution for particles detected by the ATOFMS at the tunnel site. This figure that the greatest overlap of single particle data with the bulk data occurs over the particle range 0.5 µm < Dp < 3 µm. This corresponds well with the modal concentration range of the metal species, therefore good correspondence in the composition seen by the two techniques should be attainable. Figure 6.8b gives the average composition of the particles detected by the ATOFMS during the same time period as the size distribution. The metals observed with the ATOFMS include Na, Mg, Al, K, Ca, Mn, Fe and Ba.
Figure 6.7. The average airborne trace element concentration at the Queensway Tunnel site, according to particle size fraction.
Figure 6.8. Particle count data obtained by the ATOFMS between 0900 hours BST on 02/07/02 and 1000 hours BST on 02/07/02 showing, (a) particle size distribution of particles detected and (b) average composition of “hit” particles.

As with the bulk data, comparison of ATOFMS particle composition obtained at Winterbourne and the Queensway tunnel shows an increase in the metals detected at the tunnel site. The most notable observation is the increase in iron detected in the tunnel. This is displayed in the ATOFMS spectra as peaks at m/z = 56/54, illustrating the presence of the two dominant iron isotopes in the positive spectrum, and also by
two peaks in the negative spectrum at m/z = -88 and -104 that represent the iron oxide clusters, FeO$_2^-$ and FeO$_3^-$. 

Another feature of this dataset is the presence of barium in both the bulk and single particle samples that was not observed in Winterbourne dataset. In Figure 6.8b barium is depicted by the peaks at m/z = 138 and 154 that represent Ba$^+$ and BaO$^+$. It was not surprising to see such a large increase in barium at this site as laboratory work investigating vehicle sources has proved that barium is a significant component in spectra obtained from brake linings. It is recognised that wear of other vehicle components may also add to the barium loadings.

6.6 PARTICLE COMPOSITION AT THE BRISTOL ROAD

Figure 6.9 shows the size distribution and concentration of selected trace elements at the Bristol Road site. The elements observed at this site display very similar patterns of size to those observed at the Queensway tunnel site. Not surprisingly the overall concentrations monitored at the roadside are almost a factor of 10 lower than those recorded in the Queensway Tunnel. Again Mg, Al, Ca, Mn, Fe, Cu, Zn, Ba and Pb are observed across most size ranges, with an additional observation of mercury in the finest size range that has not previously been observed in this campaign. A number of species again show bimodal distributions, including Al, Mn, Fe and Cu illustrating that there may be multiple sources contributing to these species. Zinc again shows a modal peak in the range < 0.5 µm, which agrees well motor vehicle emission studies that have shown that Zn concentrations are higher in fine particles than in the coarse particle fraction (Huang et al., 1994).
Typical results obtained from analysis of single particle data collected at the Bristol road site are given in Figure 6.10a. It should be noted that difference in the distribution of fine particles observed at here compared to those in Figures 6.6 and 6.8 is due to the presence of a new detection laser that was operating at full power, therefore allowing more finer particles to be detected and analysed. This results in a slight increase in the overlapping size range between bulk and single particle methods. Figure 6.10b gives the average composition of particle analysed by the ATOFMS over one four-hour period. The characteristic composition of particles collected at this site is the mixing of peak combinations that was found at the Winterbourne site and at the Queensway site. For example, peaks at m/z = 46, 63, 81/83, -35/-37 and -95 are all representative of either sodium, chloride or their clusters that were detected at Winterbourne. Characteristic features from the Queensway tunnel are also observed in the form of the metals that were observed with the ATOFMS, such as barium and barium oxide, iron and iron oxide, and aluminium.
Figure 6.9. The average airborne trace metal particle concentration at the Bristol Road site, according to particle size fraction.
Figure 6.10. Particle size data obtained by the ATOFMS between 0900 hours BST on 11/07/02 and 1200 hours BST on 11/07/02 showing, (a) particle size distribution of particles detected and (b) average composition of “hit” particles.
6.7 COMPARISON OF SIZE-SEGREGATED PARTICLES AT THREE BIRMINGHAM SITES

6.7.1 INTRODUCTION
This section compares the composition of size-segregated particles at three measuring sites in Birmingham: Queensway Tunnel, Bristol Road and Winterbourne. Each data set comprises data measured between 8 and 9 am but on separate days. This hour data set was selected as it represents one of the peak commuting times for people travelling into Birmingham City Centre. The results should therefore be characteristic of highly traffic-influenced environments. The spectra from the Queensway Tunnel will be taken as representative of exhaust and non-exhaust traffic-emitted particulate matter, whilst the Bristol Road data are a combination of local traffic and urban background, which Winterbourne is a background comparison site. The results from all sites will first be considered separately then a comparison will be made.

6.7.2 Queensway Tunnel
Figure 6.11a shows the average spectrum for the finest size fraction that can be measured by the ATOFMS, $0.2 \, \mu m < Dp < 0.3 \, \mu m$. It shows that the composition of this size fraction is strongly dominated by carbon containing particles. It is not unusual to observe carbon containing spectra with the ATOFMS, but what is unusual is presence of the longer $C_n^+$ chains where $n > 10$. Laboratory work that has been carried out regarding exhaust and non-exhaust traffic sources indicates that when long carbon chains are detected like this the most probable source is from diesel vehicles.

If Figure 6.11a is compared to Figure 6.11b a dramatic change in composition is observed. Figure 6.11b illustrates the average composition of particles in the diameter range, $0.3 \, \mu m < Dp < 0.4 \, \mu m$. The first observation to make is the lack of long $C_n$
chains in the negative and positive spectra. Instead only the smaller C_n chains are observed (n = < 8), with the peaks at m/z = 12 and 36 being dominant. With regards to carbon containing species, the presence of peaks at m/z = 203 and 220 should be noted. These peaks are attributed to polycyclic aromatic hydrocarbons (PAHs), and have also been observed during laboratory work using test diesel engines. Another observation in this size range is the increased presence of metals such as sodium (m/z = 23), aluminium (m/z = 27), potassium (m/z = 39) and calcium (m/z = 40). The negative spectrum illustrates an increase in nitrogen containing species such as CN⁻, NO₂⁻ and NO₃²⁻ occurring at m/z = 26, 46 and 62 respectively. There is also a prominent signal at m/z = 97 representing HSO₄⁻.

As the particle size increases from 0.4 µm to 0.7 µm the overall composition does not dramatically alter, although the intensities of a number of peaks including sodium, potassium and CN⁻ have increased in proportion to others present. Peaks around m/z = 178, 191, 206 and 220 again show that there remains a contribution from diesel vehicles in this size range, as shown in Figure 6.11c.

A dramatic difference in composition is observed for the coarser size fractions as demonstrated in Figure 6.11d which represents the average composition of particles in the size range 0.7 µm < Dp < 1.0 µm. The most noticeable differences seem to occur in the positive spectra that have become increasingly dominated by metal cations; sodium, calcium, iron (m/z = 56) and barium (m/z =138) . These peaks are more characteristic of mechanically generated particles and laboratory evidence suggests that one of the main sources of barium is from the erosion of brake linings. It should be noted that even though the overall composition of these coarser particles suggest
they have been produced by mechanical means, the observation of the PAHs show that some coarser particles result directly or indirectly from exhaust emissions. If the composition of the most coarse particles detected by the ATOFMS, shown in Figure 6.11e, are compared it is found that the average composition does not alter markedly from particles in the size range $0.7 \mu m < D_p < 1.0 \mu m$.

Figure 6.11. Composition of size segregated particles detected in the Queensway Tunnel

(a) Average composition of particles in the size $0.2 \mu m < D_p < 0.3 \mu m$. 

(b) Average composition of particles in the size $0.3 \mu m < D_p < 0.4 \mu m$. 

(c) Average composition of particles in the size 0.6 µm < Dp < 0.7 µm.

(d) Average composition of particles in the size 0.7 µm < Dp < 1.0 µm.
6.7.3 **Bristol Road**

Figure 6.12a shows the composition of the finest detectable size fraction as measured by the ATOFMS. The positive spectrum has fairly strong peaks at m/z = 12 and 36 showing that these particles contain carbon containing species. The pattern seen in the positive is characteristic of particles containing longer carbon chains too, but the intensities are very low indicating this is characteristic of only a few particles. The peak at m/z = 202 also shows that some particles are a result of PAH containing vehicular emissions. The positive spectrum also shows the presence of some metal ions with aluminium and potassium being the most abundant. In the negative spectrum intense nitrogen-containing peaks at m/z = -26, -46 and -62 have been detected showing that a high percentage of the finest particles are nitrogen rich. The peak at m/z = -97 demonstrates that sulphate is also a major constituent. The constituents sulphate and nitrate are typical of accumulation mode particles.
In the next largest size fraction ($0.3 \mu m < Dp < 0.4 \mu m$) the majority of particles contain carbon chains, as shown in the positive spectrum in Figure 6.12b. The negative spectrum again shows these particles to be nitrogen and sulphur rich.

Figure 6.12c demonstrates that as the particles get coarser, an increase in metal content is observed. In this size fraction the presence of sodium, aluminium, potassium, iron and barium are observed. These ion combinations regularly occurred in the brake lining fingerprint spectra generated in the laboratory but some can also be characteristic of crustal origins. A number of iron clusters are also seen at $m/z = 113/115$ and a peak at $-88$ represent the two potassium isotope clusters, $[^{39/41}KCl_2]$ and the iron oxide, $FeO_2^-$, respectively.

In the size range $0.7 \mu m < Dp < 1.0 \mu m$ the most notable feature is the very intense sodium, calcium and iron signals showing that the majority of these particles are dominated by the presence of these metals, as in Figure 6.12d. This combination of peaks represents particles originating from crustal sources. For particles in the size ranges $1.0 \mu m < Dp < 2.0 \mu m$ and $Dp > 2.0 \mu m$ illustrated in Figures 6.12e and 6.12f positive spectra are completely dominated by metal ions and any remnants of carbon species that could be observed have disappeared. The peak at $m/z = 81/83$ are representative of the sodium chloride clusters $[Na_2^{35}Cl]^+$ and $[Na_2^{37}Cl]^+$ that occur with a similar intensity as the metal ions. The negative spectra show that these coarse particles are heavily dominated by the presence of nitrates and chloride containing spectra. The patterns obtained here suggest that these are characteristic of aged sea-salt particles.
Figure 6.12. Composition of size segregated particles detected at the Bristol Road site.

(a) Average composition of particles in the size $0.2 \mu m < D_p < 0.3 \mu m$.

(b) Average composition of particles in the size $0.3 \mu m < D_p < 0.4 \mu m$. 
(c) Average composition of particles in the size $0.4 \, \mu m < D_p < 0.5 \, \mu m$.

(d) Average composition of particles in the size $0.7 \, \mu m < D_p < 1.0 \, \mu m$. 

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(e) Average composition of particles in the size $1.0 \ \mu m < D_p < 2.0 \ \mu m$.

(f) Average composition of particles in the size $D_p > 2.0 \ \mu m$.

6.7.4 Winterbourne

The first major observation to be made at the Winterbourne background site was the severe lack of particles in the smallest size fractions. Figure 6.13a shows the average spectrum for the first size fraction of particles observed, $0.7 \ \mu m < D_p < 1.0 \ \mu m$. The
number of particles that fell into this size fraction was minimal, with only 5 particles being allocated. Investigation of these particles showed that most contained carbon. This is also seen in the average positive spectrum in Figure B6.13a by the m/z = 12 and 36 peaks. The negative spectrum also shows carbon containing peaks, CN⁻ and CNO⁻ at m/z = -26 and -42.

The 1.0 \( \mu \text{m} < Dp < 2.0 \mu \text{m} \) size fraction accounts for 36% of the particles measured. Figure 6.13b shows the average spectrum for this size group, which contains a number of peaks that have not been described previously, e.g. m/z = 63, 81/83 and -93/-95. These peaks can be accounted for by taking into consideration the other peaks present in the spectra and the ratios of peaks intensities that are occurring. For example Figure 6.13c gives an example of an individual spectrum showing an intense peaks at mass-to-charge ratios 23 and -35. These indicate that the particle is rich in sodium and chloride and therefore it would not be surprising to observe sodium chloride clusters. In fact, these are observed in both positive and negative channels at m/z = 81/83 and -93/-95/-97, which represent the clusters \([\text{Na}_2^{35}\text{Cl}]^+/[\text{Na}_2^{37}\text{Cl}]^+\) and \([\text{Na}^{35}\text{Cl}_2]/ [\text{Na}^{35/37}\text{Cl}_2]/ [\text{Na}^{37}\text{Cl}_2]^−\) respectively. The peak at m/z = 63 is also probably due to a sodium complex for example, \([\text{Na}_2\text{OH}]^+\). A similar pattern is seen in the coarser size fraction where \(Dp > 2.0 \mu \text{m} \), shown in Figure 6.13d. These particles also show very intense nitrite and nitrate signals.
Figure 6.13a. Composition of size segregated particles detected at the Winterbourne site

(a) Average composition of particles in the size range $0.7 \mu m < D_p < 1.0 \mu m$.

(b) Average composition of particles in the size range $1.0 \mu m < D_p < 2.0 \mu m$. 
(c) Single mass spectrum for a 1.97 µm particle.

(d) Average composition of particle in the size range Dp > 2.0 µm.

6.8 SOURCE APPORTIONMENT

Initial source apportionment has been carried out on the Queensway Tunnel and Bristol Road datasets. This was accomplished by applying what has been learnt about the composition of brake, diesel, soil and tyre particles. All these particle types were
generated and analysed under laboratory conditions using the ATOFMS, enabling a unique set of fingerprints for each of these sources to be obtained, as outlined in Section 7. Each source may have several subclasses depending on how variable the spectra are from that single source, for example, 9 brake classes were required to classify the brake particles illustrating that the composition of the these particles varied greatly. The results of this exercise appear in Figure 6.14.

Figure 6.14. Results of classifying a subset of data take from the Queensway and Bristol Road datasets according to laboratory fingerprints.

The results gained from this procedure produced some unexpected results. For example, only 2% of the Queensway data were classified as tyre particles compared to a huge proportion of 18% at the Bristol Road. It is expect that all vehicle-emitted particles should decrease under more open roadside conditions, therefore this observation is very unexpected. To explain this observation a closer look at the population of the individual subclasses that are used to classify tyre particles is required. Results of this are given in Figure 6.15. These show that the most populated class at the roadside is the Tyre 1 class followed by the Tyre 2 class. The
characteristics of these classes are the presence of peaks at $m/z = 51$ and 63. Past
studies, have shown these peaks occur in other sources, for example, $m/z = 63$ was a
major constituent of aerosol collected during a field campaign conducted at Mace
Head, Ireland. This is a rural coastal site where influence from traffic sources is
minimal. This peak is usually designated as $\text{Na}_2\text{Cl}^+$ and is characteristic of clean and
aged sea salt aerosols. Figure 6.16 displays example of spectra that fall into the Tyre
1/3 classes. These spectra do not suggest a sea salt source due to the absence of
sodium and other sodium chloride clusters as well as the fine particle fraction that
they occur in. At present an exact source of these particles cannot be ascertained
though the fieldwork here suggests that they are not vehicle emitted. The presence of
a large potassium peak and also potassium clusters at $m/z = 104$ and 113/115 may
suggest a biogenic source.
Figure 6.15. The classification results for each subclass for data collected at the road tunnel and roadside site.

**Queensway**
Total particle number = 1086

**Bristol Road**
Total particle number = 338
Another point to note is the trend observed in particles classified as brake particles. Figure 6.15 reveals that large percentage of particles classes due to a brake source occur in the Brake 9 subclass. The characteristic feature of this class is the presence of iron. It is thought that classified particles here may not all be due to the wearing of brake linings, but also due to wear of other vehicle components. It is important to note that the results obtained for the tunnel and roadside do reflect that on the whole these iron particles are traffic-emitted.
A positive observation from applying this classification procedure is the reduction in diesel emitted particles at the roadside to 2% from 10% at the tunnel site. The fact that the diesel particles show the accepted trend indicates that other sources to the diesel fingerprints are low.

Overall, this brief classification example illustrates how the ATOFMS can be used as a source apportionment tool. It also indicates that a lot more fingerprinting of many different sources is required to provide better results.
7.  FINGERPRINTING ANALYSIS OF AIRBORNE PARTICLES

7.1  INTRODUCTION

Numerous studies have been conducted regarding traffic-emitted pollutants with many investigations focusing on exhaust emissions (Bukowiecki et al., 2002; Roosli et al., 2001). However, in recent years attention has turned to other traffic generated particulate sources (Rogge et al., 1993a; Weckwerth, 2001). Not only are there contributions from the tail pipes of vehicles, but also particles produced mechanically by the wearing of tyres, clutches, brake linings and road surfaces along with the corrosion of chassis, bodywork and other car components. These particles can be deposited onto the road surface along with soil and plant materials, which are pulverized and resuspended by passing traffic.

It has been shown that a significant amount of coarse material above urban background is derived from resuspension of road surface dusts (Manoli et al., 2002). It has also been suggested that these particles can lead to the production of a significant amount of fine particulate matter (Fauser et al., 2002). An inventory of fine particulate organic carbon (OC) emissions in the Los Angeles area suggest that road dust is the third largest source of fine OC matter to the urban atmosphere (Hildemann et al., 1991). Such statements indicate that long-range transport of these particles might be possible and they could have a detrimental effect on the health of animals and humans. Hence, it is necessary to find the chemical composition of resuspended road dust and the relative contribution from each source.
In this study single particle mass spectrometry (SPMS) is used to characterise individual particles that are emitted from a selection of traffic-generated sources. The major aims of this aspect of work are to:

- Determine characteristic combinations of chemical components to establish chemical markers for each source ie. Fingerprinting;
- Develop an LDI-MS (laser desorption/ionsation mass spectrometry) database for a variety of atmospheric components;
- Produce laboratory generated training sets that can be engaged in pattern recognition algorithms;
- Assist in source apportionment of atmospheric data.

Investigations characterising tail-pipe emissions have previously been carried out by the aerosol time-of-flight mass spectrometer (ATOFMS) (Silva and Prather 1997; Gross et al., 2000a). In these investigations particles were sampled from vehicles under test conditions and under atmospheric conditions in a road tunnel. In this section, new laboratory measurements from tyre wear particles, brake dust, petrol and diesel particles are reported. The fingerprints obtained in these measurements are then used to aid in the initial source apportionment of particles found in samples of road dust and in the atmosphere.

7.2 EXPERIMENTAL METHODS

7.2.1 Aerosol Time-of-Flight Mass Spectrometry (ATOFMS)

The experimental configuration of the aerosol time-of-flight mass spectrometer (ATOFMS) has been described in great detail by previous authors (Gard et al., 1997; Wood and Prather, 1998) and will only be reviewed briefly here. Particles are
sampled from atmospheric conditions through a nozzle and two differentially pumped skimmers, removing the excess gas molecules whilst collimating the particles into a narrow beam. The particles are detected and aerodynamically sized by two orthogonal continuous-wave argon lasers. The time taken for a particle to move between the lasers is monitored by a logic circuit, which controls the desorption/ionisation laser Nd:YAG laser (266 nm), firing the laser when the particle enters the centre source region. The positive and negative ions produced are separated by a time-of-flight mass spectrometer (TOFMS) with ions of different mass to charge ratios (m/z) reaching the detector at different times.

7.2.2 Sample Collection

Atmospheric Aerosol

Atmospheric samples were collected at three sites in Birmingham, UK using the ATOFMS. The first site was located in the Queensway tunnel, a major through route that transports traffic through Birmingham city-centre. Sampling lasted for 14 hours starting at 6 am and finishing till 8 pm. The second site was on the A38 Bristol Road in Bournbrook, a busy, open dual carriageway with the ATOFMS positioned in the University grounds so that the ATOFMS was elevated above the pavement. On this occasion monitoring lasted for 5 continuous days from 8\textsuperscript{th} July to 12\textsuperscript{th} July. The final site was located at Winterbourne, a background site that was approximately 200 metres away from the nearest road. During all measurements the ATOFMS was deployed in a van with a stainless steel line that carried the aerosol directly into the ATOFMS inlet.
Road Dust

Road dust was collected at both sampling sites described above. Both samples were screened with a 250 µm mesh sieve then put into clean PFDE 60 ml bottles. The finer road dust was sampled by adding a small amount to a test tube then resuspending the dust by either blowing air across the surface of the sample or by agitating it slightly. For means of comparison road dust samples were also collected during the winter after a period of icy conditions had prevailed.

Soil Particles

Soil samples were collected from the area surrounding the Bristol Road site and the Winterbourne site. Before analysis took place each sample was screened using a 250 µm mesh sieve then put into clean PFDE 60 ml bottles. The samples were sampled in a similar manner to the road dust by adding a small amount to a test tube then resuspending by blowing air across the surface or by agitating the test tube.

Brake Dust

Two separate methods were employed to sample brake dust. Method 1 involved brushing the dust that had accumulated behind the hubcap of the front wheel into a clean 5ml polyethylene bottle. A similar sampling method was used by Hilderman et al. (1991) who took brake dust samples directly from a car fitted with a brake drum. Method 2 used a steel brush powered by an electric drill to abrade the surface of the brake lining. The choice of brake pads to sample is made particularly difficult by the huge range of brake pads used on vehicles. Further complications are caused by the car manufacturers who fit several different makes of brake pads depending on the make/model of car, as well as the number of options available to car owners who need
to replace old pads including; original car dealer, speciality car repair centres (e.g. Kwik-Fit) and do-it-yourself pads purchased from car suppliers (e.g. Halfords). To simplify the selection process results from the SMMT (Society of Motor and Manufacturing Traders) Motor Industry Facts annual report 2002 (SMMT, 2002) were used, which reported that the 10 best selling cars for 2001 in the United Kingdom were:

1. Ford Focus
2. Vauxhall Astra
3. Ford Fiesta
4. Peugeot 206
5. Vauxhall Corsa
6. Ford Mondeo
7. Renault Clio
8. Renault Megane
9. Volkswagon Golf
10. Citroen Xsara

In this survey samples were collected from five cars depending on which were most readily available; therefore the samples were taken from the following models of car Ford Fiesta, Vauxhall Corsa, and Renault Clio. all of which had been supplied by the relevant car dealer. Unfortunately samples from the Vauxhall Astra and Peugeot 206 were not available so samples from other models had to be used; Vauxhall Vectra and Peugeot 306. Table 7.1 details the origin i.e. make/model of car fitted on and the
make of brake if known. The finer resuspendable brake dust was sampled using the same method as described above for the road dust.

Table 7.1. List of brake linings tested detailing the make of brake lining (if known) and make/model of car it was supplied from.

<table>
<thead>
<tr>
<th>Car Make</th>
<th>Car Model</th>
<th>Brake manufacturer</th>
<th>Brake Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peugeot</td>
<td>306</td>
<td>Girling</td>
<td>disc</td>
</tr>
<tr>
<td>Ford</td>
<td>Fiesta</td>
<td>Bendix</td>
<td>disc</td>
</tr>
<tr>
<td>Renault</td>
<td>Clio</td>
<td>Girling</td>
<td>disc</td>
</tr>
<tr>
<td>Vauxhall</td>
<td>Vectra</td>
<td>Lucas</td>
<td>disc</td>
</tr>
<tr>
<td>Vauxhall</td>
<td>Corsa</td>
<td>Unknown</td>
<td>drum</td>
</tr>
</tbody>
</table>

Tyre Particles

Tyre wear particles were sampled by simulating the abrasion process by holding the surface of the tyre next to a hand held grinder. This method produced a lot of thermal energy causing a high percentage of the fine mist of particles to heat up and adhere to the surface of the collection vessel. For this reason the abrasion method described for the brake pads was also tested, a method that was also adopted by Camatini et al. (2001). This produced much coarser particles with a lot less thermal energy. A further problem arose when attempting to resuspend the particles, which became charged causing them to stick to the walls of the sampling vessel and each other. Rogge et al. (1993a) had previously encountered this phenomenon causing them to abandon sampling fine particles and instead concentrate on characterising coarse particles only. In this work, the problem was tackled by immersing the tyre particles in methanol allowing the hydrophobic particles to disperse. The particles were then nebulised using an Acorn II nebuliser. The aerosol produced was passed through an aerosol drier containing silica beads before entering the mass spectrometer (MS) to be analysed. Using the later abrasion method, three different brands of tyres were
analysed. The brands chosen were Pirelli, Michelin and Bridgestone, which were selected according to the listed top 10 tyre manufacturers in the UK and availability.

*Leaf/Plant Debris*

Plant debris close to our sampling site on the Bristol Road was collected. Before analysis the sample was dried in an oven at 100°C to remove any excess water. A pestle and mortar was used to pulverise the debris into a fine powder and any remaining large particles were removed using a 250 µm mesh sieve to prevent larger particles from clogging the inlet system of the SPMS. The fine particles were resuspended into the MS using the method described for the brake dust.

*Diesel Exhaust*

Sampling took place with the co-operation of the Future Power Systems Group based in the School of Mechanical and Manufacturing Engineering at the University of Birmingham. The engine employed in this study was an air-cooled single cylinder four stroke, direct injection Lister Petter TR1 diesel engine. The general specifications include: Bore 98.4 mm, Stroke 101.6 mm, Capacity 773 cm³, and Compression ratio 15.5:1. For this study the fuel used was Ultra Low Sulphur Diesel (USLD). The fuel properties are listed in Table 7.2 (Teo et al., 2002).

<table>
<thead>
<tr>
<th>Fuel Analysis</th>
<th>Method</th>
<th>Ultra Low Sulphur Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Number</td>
<td>ASTM D613</td>
<td>53.9</td>
</tr>
<tr>
<td>Density at 15°C (kg/m³)</td>
<td>ASTM D4052</td>
<td>827.1</td>
</tr>
<tr>
<td>Viscosity at 40°C (CST)</td>
<td>ASTM D445</td>
<td>2.467</td>
</tr>
<tr>
<td>90 % distillation (°C)</td>
<td>ASTM D86</td>
<td>329</td>
</tr>
<tr>
<td>Sulphur (mg/kg)</td>
<td>ASTM D2622</td>
<td>46</td>
</tr>
</tbody>
</table>
A sampling line of 4 metres length carried the exhaust gas from an inlet in the side of the exhaust to the ATOFMS. Before entering the instrument the gas was passed through a condenser to remove excess water and then through a diluter so that the number of particles entering the ATOFMS was reduced by a factor of 10.

Petrol Particles
Two methods were employed for the collection of petrol exhaust particles. The first took place in the School of Mechanical and Manufacturing Engineering and employed a static petrol engine that could be tested under varying loads and speeds. Particles were sampled into the ATOFMS via a sampling line of about 3 metres that passed from an inlet on the side of the exhaust to the ATOFMS. To aid prevention of condensation occurring, the gas was passed through a diluter that reduced the particle numbers by approximately a factor of 10. A number of problems were encountered during these measurements including condensation of gases in the sampling tube and low particle numbers in the size range of the ATOFMS. For comparison, a second method was tested; sampling directly from a car exhaust. Before sampling into the ATOFMS the gaseous emissions were expanded into a sampling chamber. A sampling line of about 2 metres carried the gas from the chamber into the ATOFMS inlet to be analysed. Again low particle counts were observed.

Data Analysis – MS Analyze
In order to obtain a true representative spectral pattern for each potential traffic source a minimum of 250 spectra were collected for all samples. The software package MS-Analyze was used to support the analysis process. A more detailed description of MS-Analyze has been given in previous publications but its primary job is to view
and calibrate each spectrum. It also provides a method for searching datasets for spectra containing any queried combination of peaks and can create average spectra for each dataset. To achieve some of the aims outlined in the introduction all spectra must be classified, firstly within their own dataset, then secondly between different datasets. Detailed selection criteria for each of the samples is given in the discussion section below. The criteria were chosen so to:

- Optimise the number of classified spectra within one sample group.
- Try to minimise the overall number of classes used.
- Only use classes that are unique for a particular sample group.

7.3 RESULTS AND DISCUSSION

Brake Dust

Average spectra for each of the 5 brake pads tested are shown in Figures 7.1 to 7.5. The first observation to make is the very strong positive sodium, potassium and iron signals present in all samples. It was not surprising to detect a strong Fe$^+$ peak considering previous brake analysis that has been undertaken gave iron concentrations in range of 115,000 – 399,000 mg/kg (Warner et al., 2000). Comparing this value with typical Na and K concentrations of 15,400 and 857 mg/kg respectively (Warner et al., 2000b), it is seen that the ATOFMS is inherently more sensitive to these ions. Therefore, it would be incorrect to use peak heights alone as a measure of elemental content. Previous studies regarding relative sensitivity factors for alkali metals (Gross et al., 2000b) have also shown a higher response for the heavier cations and indicated that peak area is consistent with the periodic trends of both ionisation energy and lattice energies of various species. The average spectra also give an indication of how diverse brake pad composition is between samples. Similar patterns are observed for
the following pairs; (a) 306 and Fiesta, (Figures 7.1 and 7.2; (b) Clio and Vectra, (Figures 7.3 and 7.4) with the Corsa (Figure 7.5) having a fairly unique spectral pattern. This observation is surprising as the Clio and 306 brake pads are both manufactured by Girling so it would have been natural to assume they would have a similar spectral pattern/composition. If the pairs of brakes are scrutinised in more detail it can be seen that a unique feature of the 306 and Fiesta is the pronounced presence of barium (m/z = 138) and barium oxide (m/z = 154) (Figure 7.6) as well as a cluster of peaks occurring around m/z 92, 93, 94, 95, 96, 97 and 98 (Figure 7.7). The large signals observed for Ba\(^+\) and BaO\(^+\) have been seen previously in field measurements by Gross et al. (2000a) along with peaks at m/z = 210 and 226 representing BaFeO\(^+\) and BaFeO\(^2+\), respectively. More traditional bulk methods for collecting PM\(_{10}\) carried out in the Los Angeles Basin region have also traced vehicular emissions as being a source of barium due to the fact that it was highly correlated with lead (R\(^2\) = 0.80) (Singh et al., 2002). Another interesting observation seen for the 306 and Fiesta was the presence of antimony and its oxides in both the positive and negative spectrum. An example of an Sb-containing spectrum is shown in Figure 7.8. The doublets at m/z = 121/123 and 153/155 in positive and negative spectra represent the isotopes of \(^{121/123}\)Sb and \(^{121/123}\)SbO\(_2\), respectively, with an additional doublet in the negative spectrum at 185/187 for SbO\(_4\)\(^-\). Antimony, which has comparable toxicological behaviour to arsenic and bismuth, has been detected previously in brake pad samples with a concentration of approximately 10,000 mg/kg. Atmospheric observations by Dietl et al. (1997) suggested that antimony emissions are closely associated with traffic. The major difference between the 306 and Fiesta samples is presence of lead isotopes (m/z = 206, 207, 208) found in the Fiesta sample (Figure 7.9). The brake samples for the Clio and Vectra also display the presence of
barium and barium oxide but the averaged peaks are not as intense illustrating a reduced number of spectra containing these peaks (Figure 7.10). A characteristic cluster of peaks at m/z –140 to –147 (Figure 7.11) is observed for the Clio and Vectra, but whereas the Clio, Vectra, 306 and Fiesta all depict unique m/z combinations, the average Corsa spectrum is not so easy to classify with the majority of peaks occurring below m/z =100 (Figure 7.12 and 7.13).

Figure 7.1. Average of 303 spectra for brake linings from the Peugeot 306.
Figure 7.2. Average of 302 spectra for brake linings from the Ford Fiesta.

Figure 7.3. Average of 264 spectra for brake linings from the Vauxhall Vectra.
Figure 7.4. Average of 263 spectra for brake linings from the Renault Clio.

Figure 7.5. Average of 254 spectra for brake linings from the Vauxhall Corsa.
Figure 7.6. Example of a particle from the Peugeot 306 sample containing barium (m/z = 138) and barium oxide (m/z = 154) ions, classified into the Ba\textsuperscript{+} class.

Figure 7.7. Example of a particle from the Peugeot 306 sample containing a cluster of peaks in the range m/z = 92 – 98, classified into the Brake PAH class.
Figure 7.8. Example of a particle from the Peugeot 306 sample containing positive and negative antimony (Sb, m/z = +/- 121/123) and antimony oxides (SbO₂, m/z = +/- 153/155, SbO₄, m/z = -185/-187), classified into the Antimony 1 and 2 classes.

Figure 7.9. Example of a particle from the Ford Fiesta sample containing isotopes of lead (m/z = 206, 207, 208), classified into the lead class.
Figure 7.10. Example of a particle from the Vauxhall Vectra sample containing barium (m/z = 138) and barium oxide (m/z = 154) ions, classified into the Ba\(^+\) class.

Figure 7.11. Example of a particle from the Renault Clio sample containing a cluster of peaks at m/z = -140 to -147, classified into Clio PAH class.
Figure 7.12. Example of a particle from the Corsa sample showing a lack of high m/z peaks.

Figure 7.13. Example of a particle from the Corsa sample showing a lack of high m/z peaks.
Allowing for all the observations described above, 10 classes, given in Table 7.3, were identified to encompass the classification of the 5 different brake pad samples. The results of this classification are shown in Figure 7.14. An inclusive classification procedures was carried out allowing spectra to fall into multiple classes, therefore showing exactly how many spectra contain the stated combination of peaks. The results highlight the similarities and differences that have already been described between brake samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Subclass</th>
<th>Selection Criteria</th>
<th>Original</th>
<th>Additional NOT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>present</td>
<td>absent</td>
<td>Diesel</td>
</tr>
<tr>
<td>Barium</td>
<td></td>
<td>138</td>
<td>220</td>
<td>115</td>
</tr>
<tr>
<td>Brake Carbon</td>
<td>138</td>
<td>-36</td>
<td>132</td>
<td>115</td>
</tr>
<tr>
<td>Brake Carbon</td>
<td>-72</td>
<td>202</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Brake PAH</td>
<td>92</td>
<td>95</td>
<td>132</td>
<td>104</td>
</tr>
<tr>
<td>Brake PAH</td>
<td>95</td>
<td>-72</td>
<td>202</td>
<td>-113</td>
</tr>
<tr>
<td>Brake Phosphate</td>
<td>-63</td>
<td>-60</td>
<td>202</td>
<td>-134</td>
</tr>
<tr>
<td>Brake Phosphate</td>
<td>-79</td>
<td>-74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antimony 1</td>
<td>153</td>
<td>155</td>
<td>202</td>
<td>104</td>
</tr>
<tr>
<td>Antimony 1</td>
<td>155</td>
<td></td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>Antimony 2</td>
<td>-151</td>
<td>-153</td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>Antimony 2</td>
<td>-153</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>63</td>
<td>108</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td>220</td>
<td>115</td>
<td>-134</td>
</tr>
<tr>
<td>Iron</td>
<td>56</td>
<td>-36</td>
<td>202**</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td></td>
<td>-48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>208</td>
<td>220</td>
<td>-117*</td>
<td></td>
</tr>
<tr>
<td>Clio PAH</td>
<td>-146</td>
<td>-147</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3. Selection criteria for the 5 brake linings tested. The original criteria represent the permutations required to classify within the same sample type. The additional NOT criteria are added so to differentiate between sources.

Key: * = m/z can be the range +/- 0.6 Da. ** = m/z can be the range +/- 1.0 Da.
Tyre Particles

Before analysing the tyre particle spectra, the results gained from nebulising pure methanol were inspected. Figures 7.15 show illustrative examples of the type of particles occurring in the first methanol-only sample, along with an average for the 132 spectra collected. As seen with the brake linings, intense Na and K signals dominate most spectra. A number of unusual peak combinations also occur at m/z = 81, 97, 113 or -79, -83, -89, -92, -94, -99 (Figure 7.15b) along with single peaks at m/z = -79, -89, -147 (Figure 7.15). The observation of these peak combinations produced 4 methanol classes. Using selection criteria it was possible to search the tyre dataset and eliminate any spectra that fell into a methanol class. This method led to 24% of the Pirelli tyre sample being disregarded. The Michelin and Bridgestone samples were analysed on a separate occasion that meant a separate sample of pure methanol had to be run. On this occasion the spectral types observed were very different to the previous methanol sample as given by the average in Figure 7.15e. It is thought that the majority of the peaks in each of the methanol samples arise due to impurities in the methanol and not from the methanol itself. The classification of this second methanol sample was much easier due to the presence of the peak at m/z = 133 that occurred in 80% of spectra. Another observation that allowed easy separation of tyre particle from methanol particles is the low intensity of the peaks that were observed with the methanol-only samples. The average spectra obtained from the abrasion of the three tyre samples are shown in Figures 7.16, 7.17 and 7.18. In comparison with the brake lining samples the tyre samples generated much more repeatable patterns, within each sample and between separate samples. Taking into consideration the 3 tyre samples, 3 main tyre classes were found. The selection criteria for these classes are outlined in Table 7.4. The first class “Tyre 1” included
spectra containing peaks at m/z = 50/51 and 62/63 (Figure 7.19a). These peaks could be interpreted as shifted carbon series, but the fact that the positioning of surrounding peaks is accurate (ie. m/z = 23, 27, 39) makes it seem somewhat unlikely that this is the case. Instead these peaks may be due to a hydrocarbon series (CₙH₂⁺). Figure 7.19b gives an example of a single spectrum that has been classified as Tyre 1, illustrating the pronounced hydrocarbon series in the positive and a mixture of organic and inorganic species (m/z = -79, -97). The second class “Tyre 2” takes account of most of the remaining spectra that have very characteristic peaks at m/z = -58 and – 134. A typical single spectrum containing these peaks are shown in Figures 7.19b and 7.19c. These demonstrate that the patterns can be fairly reproducible containing strong chlorine signals and the peak at m/z = -58 most probably representing NaCl.

Table 7.4. Selection criteria for the 3 tyre classes. The original criteria represent the permutations required to classify within the same sample type. The additional NOT criteria are added so to differentiate between sources.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Subclass</th>
<th>Selection Criteria</th>
<th>Original</th>
<th>Additional NOT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Selection Criteria</td>
<td>present</td>
<td>absent</td>
</tr>
<tr>
<td>Tyre</td>
<td>1</td>
<td></td>
<td>51</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>-58</td>
<td>-134</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>39</td>
<td>51</td>
</tr>
</tbody>
</table>

Key: * = m/z can be the range +/- 0.6 Da. ** = m/z can be the range +/- 1.0 Da
Figure 7.14. Classification results using criteria given in Table 7.3 for the five samples of brake linings tested. Inclusive classification was carried out for all samples.
Figure 7.15a. Example of a methanol-only single particle mass spectrum.

Figure 7.15b. Example of a methanol-only single particle mass spectrum.
Figure 7.15c. Example of a methanol-only single particle mass spectrum.

Figure 7.15d. Example of a methanol-only single particle mass spectrum.
Figure 7.15e. Average of 130 spectra generated from a second methanol-only sample.

Figure 7.16. Average of 659 spectra obtained from drill generated Pirelli tyre particles.
Figure 7.17. Average of 220 spectra obtained from Bridgestone tyre particles.

Figure 7.18. Average of 164 spectra obtained from Michelin tyre particles.
Figure 7.19a. Example of a tyre particle that was classified into the “Tyre 1” class due to the presence of peaks at m/z = 51 and 63.

Figure 7.19b. Example of a tyre particle that was classified into the “Tyre 2” class due to the presence of peaks at m/z = -58 and -134.
The classification results are summarised in Figure 7.20, with the majority of spectra falling into the Tyre 1 class. If the materials used to manufacture tyres are considered this is not surprising result. These are as below:

- Synthetic rubber
- Natural rubber
- Sulfur and sulfur compounds
- Silica
- Phenolic resin
- Oil: aromatic, naphthenic, paraffinic
- Fabric: polyester, nylon, etc
- Petroleum Waxes
- Pigments: zinc oxide, titanium oxide, etc
- Carbon black
The major classes of materials by weight for a car tyre are typically:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>14%</td>
</tr>
<tr>
<td>Synthetic rubber</td>
<td>27%</td>
</tr>
<tr>
<td>Carbon black</td>
<td>28%</td>
</tr>
<tr>
<td>Steel</td>
<td>14-15%</td>
</tr>
<tr>
<td>Fabric, fillers, accelerators, Antioxidants, etc</td>
<td>16-17%</td>
</tr>
<tr>
<td>Average weight</td>
<td>New 25 lbs, Used 20 lbs</td>
</tr>
</tbody>
</table>

This listing show that at least 69% of the weight of a car tyre is composed of carbon or its compounds. The synthetic rubber present is usually styrene-butadiene rubber (SBR), butadiene (BR), or polyisoprene (IR) or a mixture. All radial tyres are made of the same rubber compounds with a mix of carbon black and silica. The carbon black makes the tyre black and rigid and the more silica present the more soft the tyre. Truck tyres usually require more natural rubber than synthetic rubber as it has a lower heat buildup, high elasticity, resilience and tackiness and therefore increases the vehicles stability / affinity for the road.

Diesel Exhaust

In total 276 spectra were collected with the diesel engine running idle (under no load) at 1500 rpm. The average spectrum given in Figure 7.21 shows the expected dominance of the $C_n$ chains in both the positive and negative spectra. This can be seen more clearly in the single spectrum in Figure 7.22. Such long, intense carbon chains have been observed before in atmospheric datasets obtained by Gross et al.
(2000a) and also sets obtained here in Birmingham. A more unusual set of peaks were seen at much higher masses in the positive at m/z = 179, 191, 206, 220 and 234. Such clusters are thought to be clusters of carbon ions due to PAH (polycyclic aromatic hydrocarbons) found in diesel. An example of a PAH-containing spectrum is displayed in Figure 7.23. The distinct lack of carbon chains usually observed should be noted. It must also be pointed out that it is very hard to provide an exact mass to charge ratio for such peaks due to difficulties that arise when trying to calibrate accurately the higher masses. This is primarily due to the lack of definite peak information (lock peaks) in this region. Gross et al. (2000a) detected similar high m/z peaks in measurements made in the Caldecott Tunnel, California. Observations here found PAH peaks occurring at m/z = 156, 178, 192, 202. In the work presented here it is thought that the PAH cluster observed is due to the presence of phenanthrene or its isomer anthracene (m/z = 178), along with its alkylsubstituted derivatives methylphenanthrene/anthracene (m/z = 192), dimethylphenanthrene/anthracene (m/z = 206), trimethylphenanthrene/anthracene (m/z = 220), and tetramethylphenanthrene/anthracene (m/z = 234). Previous investigations into the organic composition of diesel and gasoline exhaust have detected phenanthrene and anthracene as important constituents (Alsberg et al., 1985; Rogge et al., 1993b; Lowenthal et al., 1994). Rogge et al. (1993b) reported emission rates for more than 30 PAH and alkyl–PAH.

The PAH/carbon series-containing spectra comprised two important classes of diesel particles that could be used for classification purposes, referred to as Diesel 1 and Diesel 2, respectively. Another two classes were needed to incorporate the remaining spectra. The Diesel 3 class included particles that had strong peaks for sulphur-
containing species, SO$_3^-$ (m/z = -80) and HSO$_4^-$ (m/z = -97) as depicted by the spectrum in Figure 7.24. The final class, Diesel 4, was another carbon-containing particle that had a strong carbon series occurring in the negative spectrum and only a large Na$^+$ peak in the positive instead of the usual analogous positive-carbon series that was seen before. An example spectrum is shown in Figure 7.25. A summary of the classification criteria for all 4 diesel classes is given in Table 7.5. The results of this classification are shown in Figure 7.26. An important point to note from these results is the exclusiveness of the Diesel 1 class, which shows that spectra that contain the PAH cluster do not also contain positive and negative carbon series.

### Table 7.5. Selection criteria for the 4 diesel classes. The original criteria represent the permutations required to classify within the same sample type. The additional NOT criteria are added so to differentiate between sources.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Subclass</th>
<th>Selection Criteria</th>
<th>Additional NOT</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>Original</td>
<td>Brakes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>present</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
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<td>206*</td>
<td>-72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>48</td>
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</tr>
</tbody>
</table>

Key: * = m/z can be the range +/- 0.6 Da. ** = m/z can be the range +/- 1.0 Da
Leaf/Plant Debris

The average spectrum for particles derived from leaf/plant debris appears in Figure 7.27. The average spectrum highlights the intense potassium signal (m/z = 39) observed in the majority of spectra, as well as a very strong peak at m/z = 40 most probably due to the presence of calcium in the sample. In the negative spectrum the fragmentation pattern is dominated by a group of peaks at m/z = -24, -25, -26. which are most probably due to the species C_2^−, C_2H− and CN− (Figure 7.28). Another dominant set of peaks occur at m/z = -42 and -43 that could represent CNO− and AlO−, respectively (Figure 7.28). The presence of these dominant peaks had not been observed in earlier samples, therefore the combination m/z = -41/-42/-43 became the selection criteria for the class “Leaf 1” (Figure 7.28). A lot of the spectra observed contained many unusual peaks that as yet have not been assigned. For example, the class “Leaf 2”, were selected from the presence of peaks occurring at m/z = -59 and –71. As reported for the brake linings (Figure 7.28) these peaks could be interpreted as being due to C_5− and C_6−, but as discussed previously the calibration for the surrounding peaks is consistent, implying that the masses assigned are correct. More unusual peaks were observed at m/z = 74, 86 and 104, which became the classification criteria for the “Leaf 3” class. No firm chemical identify has been assigned to these peaks but their occurrence seems to be interrelated. This can be seen in the individual spectra displayed in Figures 7.29a,b. The classification results in Figure 7.31 show that 14% of spectra contain these peaks indicating that this pattern of peaks is fairly important in characterising this sample type. The final two classes, “Leaf 4” and “Leaf 5” contained those particles containing phosphate peaks at m/z = -63, -79 (Figure 7.29b) and spectra containing peaks at m/z = -17, -26 and –42 (Figure 7.30), respectively. The “Leaf 5” class was mainly chosen so to increase the
total number of particles classified in this dataset. The classification criteria are reviewed in Table 7.6.

Table 7.6. Selection criteria for the 5 leaf/plant debris classes. The original criteria represent the permutations required to classify within the same sample type. The additional NOT criteria are added so to differentiate between sources.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Subclass</th>
<th>Selection Criteria</th>
<th>Additional NOT</th>
<th>Diesel</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Original</td>
<td>present</td>
<td>absent</td>
</tr>
<tr>
<td>1</td>
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<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-42 (&gt;75)</td>
<td>51</td>
<td>121</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>-59</td>
<td></td>
<td>-146</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>-63</td>
<td>36</td>
<td>56 (&gt;100)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>-17</td>
<td>36</td>
<td>27 (&gt;100)</td>
</tr>
</tbody>
</table>

Key: * = m/z can be the range +/- 0.6 Da. ** = m/z can be the range +/- 1.0 Da

Soil Particles

Figures 7.32a and b illustrates the average spectra for soil samples gathered at the Bristol Road site and at the Winterbourne site. The averages indicate that that the difference between the two soil samples as measured using SPMS is almost
negligible. Both soil samples contain a range of metal components, the most intense peaks being lithium, sodium, aluminium, potassium/calcium and iron at m/z = 7, 23, 27, 39/40 and 56. These peaks are the dominant members of the positive spectra, with a smaller peak in the Bristol Road sample at higher mass-to-charge ratios representing lead at m/z = 208. The negative spectra also exhibit a dominant set of peaks occurring at m/z = -17, -26, -42, -63 and –79. These illustrate the presence of OH⁻, CN⁻, CNO⁻, PO₂⁻ and PO₃⁻. The combination of the strong CN⁻ and phosphorus containing species seem to be unique to these soil samples with only the biogenic plant debris giving similar peak combinations. The strong metal peaks, although very characteristic of these soil patterns, would not make as a good tracer for soil samples as these also occur often in the brake lining samples. For this reason selection criteria dominated by the presence of CN⁻ and phosphate species were used to classify the particles. The exact selection criteria are given in Table 7.7 with typical spectral examples shown in Figure 7.33. The results of the classification process are given in Figure 7.34, and show that the majority of spectra are classed into the subclass Soil 1.

Table 7.7. Selection criteria for the 3 soil classes. The original criteria represent the permutations required to classify within the same sample type. The additional NOT criteria are added so to differentiate between sources.

<table>
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<th>Subclass</th>
<th>Original Selection Criteria</th>
<th>Additional NOT Criteria</th>
</tr>
</thead>
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<td>138 -147 -63</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-63 -26 -79</td>
<td>138 -147 -12 -63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-150</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-17 -26 -42</td>
<td>138 -147 -12 -63</td>
</tr>
</tbody>
</table>

Key: * = m/z can be the range +/- 0.6 Da. ** = m/z can be the range +/- 1.0 Da
Petrol Exhaust

Examples of typical petrol exhaust particle data are illustrated in Figure 7.35. Classification of these data has not been accomplished. Further studies are required as very few particles were collected during these experiments and additional measurements will be made to verify their composition. Results so far indicate that the composition of petrol particles is very different to the diesel particle composition that has been observed in this work. No strong carbon chains are evident in the petrol spectra instead peaks at m/z = 12, 23, 27, 39 and 56 show the presence of carbon, sodium, aluminium, potassium and iron in the positive whilst the negative spectra indicate a mix of carbon and nitrate/phosphate/sulphate species.

7.2.3 Conclusion

This paper demonstrates how the ATOFMS can be employed to characterise particles derived from a range of vehicular sources. Using the combination of positive and negative spectra unique m/z permutations can be assigned to each vehicular source as shown in Tables 7.3-7.6. The classification results show that spectra can be sorted and assigned to specific sources according to the peaks present and absent. By applying these chemical marker combinations to atmospheric samples, it should be possible for specific sources to be identified and quantified. The data collected also provide a preliminary LDI-MS library of vehicular and non-vehicular atmospheric sources that can supply training sets for developing an automated classification system (eg. neural networks).
Figure 7.20. Classification results using criteria given in Table 7.4 for the 3 brands of tyre generated particles.

Figure 7.21. Average of 276 spectra produced from a diesel engine running idle at 1500 rpm using Ultra Low Sulphur Fuel.
Figure 7.22. A typical spectrum of a diesel exhaust particle illustrating the presence of long chain carbon series (A "Diesel 2" classed particle).

Figure 7.23. A typical PAH-containing spectrum of a diesel exhaust particle. (A "Diesel 1" class particle).
Figure 7.24. An example of a typical particle that was classified as a “Diesel 3” type particle having peaks at $\text{SO}_3^-$ (m/z = -80) and $\text{HSO}_4^-$ (m/z = -97).

Figure 7.25. An example of a typical particle that was classified as a “Diesel 4” type particle having a carbon series in the negative and a sodium peak in the positive.
Figure 7.26. Classification results using criteria given in Table 4 for the diesel exhaust particles. Inclusive classification was carried out.

Figure 7.27. Average of 254 spectra for a sample of leaf/plant debris.
Figure 7.28. An example of a leaf/plant particle belonging to the class “Leaf 1”. Note the dominant signals at m/z = -24, -25, -26, -42, and –43.

Figure 7.29a. An example of a leaf/plant particle belonging to the class “Leaf 3”. Note the pattern of signals at m/z = 74,104.
Figure 29b. An example of a leaf/plant particle belonging to the class “Leaf 4”. Note the pattern of signals at m/z = 74, 86, 104.

Figure 7.30. An example of a leaf/plant particle belonging to the class “Leaf 5”.

Figure 7.31. Classification results using criteria given in Table 7.6 for leaf/plant debris particles. Inclusive classification was carried out.

![Bar chart showing classification results for leaf/plant debris particles.]

Figure 7.32a. Average of 256 spectra obtained from a soil sample from the Bristol Road site.

![Graph showing average of 256 spectra.]
Figure 7.32b. Average of 255 spectra obtained from a soil sample from the Winterbourne site.

Figure 7.33a. Example of an individual spectrum typical of the soil 1 class.
Figure 7.32b. Example of a soil particle belonging to the Soil 2 class.

Figure 7.33c. Example of a soil particle belonging to the Soil 3 class.
Figure 7.34. Classification results using criteria given in Table 7.7 for soil particles.

![Classification results diagram](image)

Figure 7.35. The average composition of particles measured from a petrol engine running at 1497 rpm.

![Composition diagram](image)
8. ACKNOWLEDGEMENTS

The authors acknowledge with thanks the contribution of the Ford Research Centre, Aachen, Germany in the loan of their mobile laboratory for field work. The individual contributions of Dr Rainer Vogt, Dr Volker Scheer and Dr Ulf Kirchner have been especially valuable. The assistance of Dr David Beddows and Dr Jacob Baker of the University of Birmingham in fieldwork and data analysis is also gratefully acknowledged.
REFERENCES


Dietl C., Reifenhauser W. and Peichl L., Association of antimony with traffic -occurrence in airborne dust, deposition and accumulation in standardized grass cultures, Science of the Total Environment, 205, 235-244, (1997).


## APPENDIX 1

Table 1. LAMPAS file list for spectra collected at the a) Regent’s Park site and b) Exhibition Road site during the winter London campaign.

**a)**

<table>
<thead>
<tr>
<th>File No.</th>
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<th>Diameter</th>
<th>Particle No.</th>
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<td>135</td>
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<td>010215c</td>
<td>2/15/01 6:57 - 2/15/01 9:53</td>
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<td>143</td>
</tr>
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<td>136</td>
</tr>
<tr>
<td>010216a</td>
<td>2/16/01 11:49 - 2/16/01 15:45</td>
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<td>127</td>
</tr>
<tr>
<td>010216b</td>
<td>2/16/01 16:38 - 2/16/01 16:56</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>010216c</td>
<td>2/16/01 17:40 - 2/17/01 0:25</td>
<td>0.7</td>
<td>81</td>
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<tr>
<td>010216d</td>
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<td>2</td>
<td>19</td>
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<td>010216e</td>
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**b)**

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APPENDIX II

A. Coarse particle composition for winter 2001 London campaign determined from Analysis of Partisol samples.

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<td>20</td>
</tr>
<tr>
<td>2/15/2001 18:05</td>
<td>25</td>
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<td>2/15/2001 22:05</td>
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B. Fine particle composition for winter 2001 London campaign determined from Analysis of Partisol samples.

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<tr>
<td>2/20/2001 12:00</td>
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C. Example of a mass distribution collected at Regent’s Park with a MOUDI impactor.

D. Example of a mass distribution collected at Exhibition Road with a MOUDI impactor.
Figure A. Classes produced from LAMPAS data obtained during London Winter campaign using selection criteria from Table 1.

(a) Aged Carbon

(b) Na-K rich
(c) Mixed Nitrate and Sulphate

(d) Secondary

(e) Nitrate only
APPENDIX IV

A. Coarse particle composition for summer 2001 London campaign determined from Analysis of Partisol samples. The date and time represent the midpoint of the 4 hour measuring period.

Anions

Cations

A. Fine particle composition for summer 2001 London campaign determined from Analysis of Partisol samples. The date and time represent the midpoint of the 4 hour measuring period.