Major component composition of PM$_{10}$ and PM$_{2.5}$ from roadside and urban background sites

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Abstract

Using dichotomous Partisol samplers, airborne particulate matter has been collected and analysed as PM$_{2.5}$ and PM$_{10}$. The instruments were deployed at four sets of paired roadside and urban background locations, three in London and one in Birmingham (UK) and the sampling protocols aimed to give equal weight to all seasons of the year. In addition to determination of sample mass, concentrations have been determined for major chemical components as follows: sulphate, nitrate, chloride, organic carbon, elemental carbon, iron and calcium. The measured concentrations have been converted to equivalent quantities of ammonium sulphate, ammonium nitrate (in PM$_{2.5}$), sodium nitrate (in PM$_{2.5}$–10), sodium chloride, elemental carbon, carbon compounds, gypsum and iron-rich dusts. The mass of strongly bound water has also been calculated following the mass closure methodology of Harrison et al. (Atmos. Environ. 37 (2003) 4927). Examination of the difference between roadside (mean 34.7 µg m$^{-3}$ PM$_{10}$) and corresponding urban background (mean 23.2 µg m$^{-3}$ PM$_{10}$) samples indicates average mass increments of 11.5 µg m$^{-3}$ of PM$_{10}$ and 8.0 µg m$^{-3}$ of PM$_{2.5}$ for the four site pairs, and that the roadside particle increment is comprised very largely of elemental carbon, organic compounds and iron-rich dusts. The major component composition lies somewhere between that reported as typical of the eastern and western US. A comparison with PM$_{2.5}$ and PM$_{15}$ sampled in Leeds (UK) in 1982 shows a decline in all major constituents except mineral dusts (PM$_{2.5}$ only). In a comparison of data for days with PM$_{10}$ above the EU 24-h Limit Value of 50 µg m$^{-3}$ with data from all days, the component showing the greatest ratio between high pollution days and all days is fine particle nitrate.

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1. Introduction

The chemical composition of airborne particulate matter in polluted atmospheres has become a topic of considerable importance over recent years, there being at least three major reasons for the attention paid to it.

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The toxicity of airborne particles is a subject of intense research interest and both epidemiological and toxicological investigations have sought to establish the chemical components primarily responsible for the toxicity (Harrison and Yin, 2000). Both major and minor components have fallen under the spotlight, and there is evidence that road traffic emissions, which in the UK are well represented by elemental and organic carbon, may be one of the more toxic particle components (Laden et al., 2000; Katsouyanni et al., 2001).
Airborne particulate matter has many sources and one means of source apportionment is through receptor modelling of atmospheric concentrations of specific chemical components which are linked to particular emission sources or secondary formation. Temporal trends in specific components may be used to evaluate the effectiveness of abatement strategies for relevant emission sectors.

At the time of writing, the USEPA has promulgated air quality standards for both PM$_{2.5}$ and PM$_{10}$ mass and is moving towards standards for PM$_{2.5}$ and coarse particles (PM$_{2.5-10}$). In the European Union, the first Daughter Directive to the Air Quality Framework Directive set air quality limit values for PM$_{10}$, but the Clean Air for Europe (CAFE) process is currently recommending a change to a PM$_{2.5}$ standard. In the context of these strict air quality standards and limit values, attention is focussing on cost-effective abatement measures, which require sound knowledge of particle source contributions to both PM$_{2.5}$ and PM$_{10}$ mass in the atmosphere. The research described in this paper was directed towards evaluating the major component composition of airborne particles in the UK and determining the roadside increment in both PM$_{2.5}$ and PM$_{10}$ at representative UK urban locations. In a collation of UK particle composition data, Harrison and Jones (1995) were able to build a picture of particle chemical composition but based on a wide range of disparate measurements. The only earlier reported attempt at accounting for the entire mass of airborne particles (i.e. mass closure) for the UK dates back to the work of Clarke et al. (1984) based on samples collected in the summer of 1982.

We have recently reported a pragmatic mass closure method derived from analysis of particulate matter collected at UK sites (Harrison et al., 2003). We now analyse the same body of aerosol data in the context of the magnitude of concentrations, the composition of the roadside increment and in a comparison with data sets from other locations and periods in time.

2. Experimental

2.1. Air sampling

Four paired roadside and urban background locations were used for air sampling as follows:

**High Holborn, London:** The sampler was located on St. Giles High Street a few metres away from one of the busiest junctions in the Borough of Camden in the commercial centre of London, and where there is a high proportion of taxis in the vehicle fleet. The site is enclosed with buildings of around five storeys on all surrounding roads. The corresponding background site was located about 300 m away in Macklin Street which is a pedestrianised area between two very quiet roads. The annual average daily traffic flow at the roadside site is 27,300 vehicles per day.

**Elephant and Castle, London:** The Elephant and Castle roadside site was located on the edge of the Elephant and Castle roundabout on the junction with St. George’s Road in a heavily trafficked part of south central London. The annual average daily traffic flow at this location is 88,500 vehicles per day. At the roundabout are junctions with five busy roads, Kensington Park Road, London Road, St. George’s Road, New Kent Road and Newington Causeway. The corresponding background site was about 500 m distant and located within a fenced garden in the grounds of the Imperial War Museum, approximately 200 m from the nearest roadside.

**Park Lane, London:** This site was located on the kerbside of a busy A4202 Park Lane Road opposite Hyde Park. The site has multistorey buildings to one side, but the road is open to the other side into Hyde Park. Annual average daily traffic flows were 104,400 vehicles per day. The corresponding background site was located within Hyde Park at a distance of 1 km from the roadside site.

**Selly Oak, Birmingham:** The roadside site was located on the kerbside of a junction of the busy A38 Bristol Road, Birmingham. To one side there are buildings of approximately three storeys whilst the terrain is relatively open and falling in altitude to the other side. The annual average daily traffic flow on the A38 road is 53,300 vehicles per day. The background side was initially located some 150 m to the east on a quiet suburban road (Katie Road).

All of the roadside samplers were located within 1 m of the kerbside. In all cases, sampling took place simultaneously at the roadside and urban background location. The original sampling protocol involved measurements of 3 weeks duration at each pair of sampling sites in each season of the year with the samplers moving between sites in between. This would have achieved the collection of eighty-four 24-h samples at each site representative of all four seasons of the year. In the event, instrument malfunctions led to frequent aborting of automatic sampling, and despite extending the sampling programme, the full number of simultaneous samples was never achieved. Rupprecht and Patashnick Dichotomous Partisol Plus model 2025 sequential air samplers fitted with PM$_{10}$ inlets at a height of 2 m with a design airflow of 16.7 l min$^{-1}$ were utilised for all air sampling. These collect a separate fine fraction (PM$_{2.5}$) and coarse fraction (PM$_{2.5-10}$), the latter contaminated with a small proportion of fine fraction particles which are subtracted in the subsequent calculations. The calculation of coarse PM is achieved...
using the formula, \( C_c = M_c / V_r - (V_c / V_t) C_t \) (where \( C_c \) is the mass concentration of the coarse particle fraction, \( M_c \) the mass collected on coarse particle fraction filter, \( V_c \) and \( V_t \) are the volumes of air sampled through the coarse fraction filters and the sum of coarse and fine fraction filters, respectively, and \( C_t \) = mass concentration of the fine particle fraction). At each site, one sampler was equipped with Whatman PTFE filters of 1 \( \mu \)m pore size and the other with Whatman QM/A quartz fibre filters of 0.6 \( \mu \)m pore size. The PTFE filters were used for the determination of particle mass concentration and for the chemical analysis of inorganic constituents whilst the quartz fibre filters were used for the analysis of organic and elemental carbon. Sampling took place over sequential 24-h intervals with filter changing normally taking place at 12 noon. Sampling took place over the period April 2000 to January 2002 and 97 sets of samples were collected in which full analytical data were available for both the roadside and background sites. However, additional single site samples have also been used in some aspects of the data analysis in this work. Concentrations refer to ambient temperature and pressure conditions without adjustment.

2.2. Analytical methods

Particulate matter mass concentration was determined by weighing of the Teflon filters using a Sartorius model MC5 microbalance before and after air sampling. All filters were equilibrated at a relative humidity of 45–55% and a temperature of 20\( \pm \)2\(^\circ\)C in the weighing room for at least 24 h before weighing commenced. An ionising blower and an \( \alpha \)-particle source were used to eliminate the effects of static electricity on the weighing process. The mass of the coarse fraction was corrected for fine fraction particles contained in the carrier flow.

One half of the PTFE filter was wetted with propan-2-ol (0.3 ml) and then extracted with distilled deionised water (10 ml) with mechanical shaking for 20 min. Dissolved concentrations of chloride, nitrate and sulphate were analysed using a Dionex DX500 chromato-graphy system with an AS4A-SC analytical column. The eluant used was a 0.1 M sodium hydroxide solution and concentrations were determined by construction of a calibration curve with standards of known concentration.

The other half of the filter was digested in a solution of mixed acid (5 ml) prepared by mixing concentrated nitric acid (65 ml), concentrated hydrochloric acid (185 ml) and dilution to 11 with distilled deionised water following the method of Harper et al. (1983). The acid extractant and filter were heated at 100\(^\circ\)C for 30 min in a water bath and then placed in ultrasonic bath at 50\(^\circ\)C for a further 30 min. This cycle was then repeated and the resulting extracts transferred to graduated flasks and diluted to 10 ml with distilled deionised water ready for analysis. Concentrations of calcium and iron were determined using a Pye-Unicam SP9 atomic absorption spectrometer with an air-acetylene flame using the 248.3 nm resonance line for iron and 422.7 nm resonance line for calcium. Calibration was with standard solutions over the range 0–10 \( \mu \)g ml\(^{-1}\), prepared in a 50:50 mixture of acid digestion solution and distilled deionised water in order to ensure matched solution matrices. Filter blanks were determined and subtracted in all analyses.

In order to minimise their carbon content, the quartz filters were preheated to 500\(^\circ\)C in air using a furnace prior to air sampling or use as an analytical blank. Analysis of carbon was by means of a Leco Instruments model RC412 carbon determinator. This instrument subjects the sample to combustion in a stream of pure oxygen in a programmable furnace. Evolved carbon dioxide is measured by infrared absorption, and carbon combusting at between 100\(^\circ\)C and 350\(^\circ\)C is attributed to organic carbon whilst combustion between 350\(^\circ\)C and 800\(^\circ\)C is indicative of elemental carbon. The instrument was calibrated using calcium carbonate as a standard and also checked against organic compounds of known composition. It is recognised that this method may lead to some mis-assignment of carbon into the elemental and organic categories particularly as a result of the conversion of organic carbon to elemental carbon by pyrolysis. However recently published laboratory inter-comparisons have failed to establish a standard procedure (Schmid et al., 2001) and recent work of Yang and Yu (2002) indicates that the commonly used optical correction technique for charring may be unreliable. Therefore our results are presented without adjustment.

2.3. Mass closure analysis

The results were subjected to our pragmatic mass closure method (Harrison et al., 2003). Briefly, it was assumed that measured sulphate is present wholly as ammonium sulphate, fine particle nitrate as ammonium nitrate whilst coarse particle nitrate is in the form of sodium nitrate. Chloride is assumed to be in the form of sodium chloride, elemental carbon as such, and the mass of organic carbon was converted to a mass of organic compounds using factors of 1.3 for roadside sites, and 1.4 for urban background. The choice of these factors is explained in Harrison et al. (2003) and is not discussed further here. Whilst it is very likely that the factors for the background and roadside sites have a seasonal dependence due to changes in the relative concentrations of primary and secondary organic compounds, in the absence of data to support the use of seasonally varied ratios these have been assumed constant through the year. Concentrations of calcium were converted to an equivalent mass of gypsum, assumed to be representative of the calcium salts present, whilst the iron was
taken as representative of soil and road dust and fitted factors of 5.5 (roadside), and 9.0 (urban background) were applied to iron concentrations to convert them to a mass of what is termed Fe-rich dust in Table 1. Janssen et al. (1997) have shown iron concentrations to be significantly higher at street sites compared to background sites. This reflects the difference in the dust composition and coarse particle sources between such sites and gives some justification for the use of different factors. The last column refers to strongly bound water which was estimated as 29% of the mass of ammonium sulphate, ammonium nitrate and sodium nitrate based on an optimisation of the fit between measured sample mass and mass reconstructed from the sum of the components. The reasoning behind this is set out more fully by Harrison et al. (2003).

3. Results and discussion

An initial appraisal of the data indicated that whilst absolute concentrations varied somewhat between the individual sampling sites of a given type, the compositional analysis did not indicate any appreciable differences in composition between the four urban background sites and between the four roadside sites. The data have therefore been averaged and appear in Table 1 as both mass concentration and percentage composition separately for urban background and roadside sites and for the difference (roadside-urban background) termed the roadside increment, which was calculated from the 97 paired roadside and background samples only. The results are presented in terms of the major chemical constituents developed in our mass closure analysis (Harrison et al., 2003).

The composition of PM10 at urban background sites (Table 1) is seen to be dominated by carbonaceous combustion particles (31.2%), secondary nitrates and sulphate (28.3%) and coarse dusts (32.3% including sodium chloride). This fits with the conceptual model developed by the Quality of Urban Air Review Group (QUARG, 1996) and the Airborne Particles Expert Group (APEG, 1999). However, the current data give a much more complete picture, including composition within those categories. As anticipated, PM2.5 is dominated by the carbonaceous combustion component and the secondary ammonium nitrate/sulphate whilst the PM2.5–10 comprises mainly sea salt and calcium and iron-rich dust components.

Rather than focusing on the roadside site data, it is more instructive to examine the roadside increment. Differences of a few percent are unlikely to be significant and hence only three components appear to account for the roadside increment, i.e. elemental carbon, organic
carbon and iron-rich dusts. It was anticipated that secondary sulphates and nitrates would not differ significantly between urban background and roadside sites as these are not generated significantly by road traffic. The possibility was considered that sodium chloride due to the use of de-icing salt might cause a positive increment at roadside sites but our data give no support for this concept. When the chloride concentration at roadside was plotted against mean daily temperature, the only trend was for an increase in chloride with temperature, thought to reflect the association of chloride with warmer, maritime air mass trajectories with stronger winds. However, the period of sampling was relatively mild, and taking account of urban heat island effects, the need for road salting is likely to have been very infrequent, and therefore even if it caused a concentration increment on a few days, is unlikely to feed through into the averaged data. Calcium is a normal constituent of soils and limestone and can also be used as a filler in road surfacing materials. It was therefore surprising that there was no consistent difference in calcium concentrations between roadside and urban background sites and the inference was drawn that the calcium more likely arises from construction and demolition activity and from resuspension of soil. The mass closure work (Harrison et al., 2003) showed that the iron content of coarse dusts was much greater at roadside than urban background (and hence the different factors used in converting the mass of iron to a mass of dust). This is indicative of road traffic, and probably the vehicles themselves, making a major contribution to the mass of coarse particles. The precise origins, be they from brake wear, corrosion or engine emissions are currently unclear.

In Table 2, the percentage composition of our samples is compared with representative data reported for the US by USEPA (1996) and UK samples of PM$_{15}$ collected by Clarke et al. (1984) in Leeds (UK) in the summer of 1982. In order to compare the data sets an ammonium concentration for our samples has been estimated from the calculated masses of ammonium sulphate and ammonium nitrate, and a concentration of minerals has been calculated. In the case of our data, the latter includes sodium chloride, calcium sulphate and iron-rich dusts together with bound water. In the case of the Leeds samples, the minerals component contains that reported originally as insoluble minerals together with the Na/K/Ca/Mg concentration. The comparison of percentage composition for PM$_{10}$ shows a major difference between the eastern and western US, with the eastern US being relatively sulphate rich, nitrate poor, and also having a lower percentage of carbonaceous aerosol and minerals than the western US. In comparison, the London and Birmingham data lie somewhere intermediate between the eastern and western US with respect to sulphate and nitrate with relatively high concentrations of carbonaceous particles and minerals more closely comparable to the western than the eastern US. The same is true of PM$_{2.5}$ composition. The table also includes data from the PM$_{15}$ samples collected by

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Comparison of particle composition (%) from the US (USEPA, 1996) and Leeds (UK) (Clarke et al., 1984) in 1982 with the London and Birmingham data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulphate</td>
</tr>
<tr>
<td><strong>US</strong></td>
<td></td>
</tr>
<tr>
<td>Eastern, PM$_{10}$</td>
<td>27.8</td>
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<tr>
<td>Eastern, PM$_{2.5}$</td>
<td>34.1</td>
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<tr>
<td>Eastern, PM$_{2.5-10}$</td>
<td>4.9</td>
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<tr>
<td><strong>US</strong></td>
<td></td>
</tr>
<tr>
<td>Western, PM$_{10}$</td>
<td>4.6</td>
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<tr>
<td>Western, PM$_{2.5}$</td>
<td>10.8</td>
</tr>
<tr>
<td>Western, PM$_{2.5-10}$</td>
<td>3.1</td>
</tr>
<tr>
<td><strong>Leeds (UK) (1982)</strong></td>
<td></td>
</tr>
<tr>
<td>PM$_{15}$</td>
<td>19.2</td>
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<tr>
<td>PM$_{2.5}$</td>
<td>26.1</td>
</tr>
<tr>
<td>PM$_{2.5-15}$</td>
<td>7.4</td>
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<tr>
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<tr>
<td>PM$_{2.5}$</td>
<td>17.7</td>
</tr>
<tr>
<td>PM$_{2.5-10}$</td>
<td>8.6</td>
</tr>
</tbody>
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$^a$Reconstructed: see text.
Clarke et al. (1984) in Leeds in 1982. To overcome problems of flow resistance, Clarke et al. (1984) applied slight warming to the inlet of their sampler which may have influenced the concentrations of semi-volatile constituents, especially fine nitrate. These data show a relative decrease in sulphate and an increase in nitrate in the London and Birmingham data relative to the Leeds data. The percentages of carbonaceous particles, minerals and chloride are remarkably similar especially given that the Leeds sample extends to 15 μm as opposed to the 10 μm of the London and Birmingham samples. The comparison is perhaps more realistic for PM$_{2.5}$ which again shows a substantial relative decrease in sulphate accompanied by an increase in nitrate, ammonium and chloride being relatively constant. The PM$_{2.5}$ shows a decreasing carbonaceous aerosol content in the London and Birmingham samples relative to Leeds but higher concentrations of minerals, although this may be an artefact of the way in which the mineral concentration has been estimated. It must be borne in mind in making this comparison that the London and Birmingham samples included all seasons of the year, whereas the Leeds samples are from the summer months only, and the nature of the sampling sites was somewhat different. However, as a broad comparison of changes in aerosol composition over some 20 years, the data should be reasonably representative. Sulphate and nitrate concentrations in the UK atmosphere do not show a strong seasonal dependence (QUARG, 1996).

Fig. 1 shows a graphical representation of changes in absolute concentrations of components from the Leeds and London and Birmingham samples. In the latter case, only summer (June–August) data have been used. Concentrations of secondary aerosol constituents should be reasonably representative irrespective of local siting of samplers, although there is a general south-east to north-west gradient in sulphate across the UK (APEG, 1999) which would imply that annual average sulphate concentrations in Leeds would be expected to be somewhat lower than in Birmingham which in turn would be expected to be lower than those in London. The spatial pattern of nitrate concentrations is less clearly known. The data show clearly a very substantial decline in absolute sulphate concentrations consistent with trends generally across western Europe as a result of reductions in sulphur dioxide emissions. There is a decline in nitrate when the summer data only are used, whereas using the full London/Birmingham data set shows only a small change in nitrate. Concentrations of carbonaceous particles have also declined quite strongly as a result of improved vehicle technologies and fuels, although local emissions make a major contribution and hence the differences in sampler siting between Leeds and the more recent work may be of some importance.

The current European Union limit value for airborne particulate matter comprises both an annual mean concentration (40 μg m$^{-3}$) and a daily concentration of 50 μg m$^{-3}$ which should not be exceeded more than 35 times per year. We have, therefore, averaged data separately for PM$_{10}$ for days with concentrations above 50 μg m$^{-3}$ and for comparison with data averaged over all days. The results which appear in Fig. 2 show for the urban background an approximate doubling of concentrations of elemental carbon, organic compounds, sodium nitrate, ammonium sulphate, calcium sulphate and iron-rich dusts on high pollution days. The most marked difference is an increase of more than five-fold in the ammonium nitrate concentration. This substance becomes the predominant component of PM$_{10}$ at urban background sites under these circumstances. When combined with sodium nitrate, it accounts for almost a quarter of aerosol mass indicating the importance of control of NO$_x$ emissions towards a reduction in PM$_{10}$ concentrations. Turning to the roadside data in Fig. 2, the high pollution days show increases of very approximately twofold in all constituents other than sodium chloride, which falls in concentration. This is clearly indicative of a mixture of events in some of which strong elevation of regional nitrate is important (based on the urban background site measurements) and other days in which the pollutants associated with road traffic.
(EC, OC and iron-rich dust) are strongly elevated due to local emissions and adverse meteorology. In comparing the urban background and roadside data sets, it needs to be borne in mind that they do not all derive from the same set of days and that the number of valid samples for the urban background measurements was 50% higher than that for the roadside data.

4. Conclusions

Data are presented for the first time from measurements of airborne particle composition at UK sites based on a mass closure method. These data clearly show an urban background aerosol made up from combustion-generated carbonaceous particles, secondary sulphates and nitrates from regional transport, sodium chloride and predominantly coarse dusts. The latter appear to have a separate calcium- and iron-rich component, the former apparently being associated with soils and construction and demolition activity, the latter having a close relationship to road traffic. The roadside sites show a strong elevation in elemental carbon, organic compounds and iron-rich dusts in comparison to the simultaneously collected urban background samples.

A comparison of particle composition with data typical of the eastern and western US shows that the UK samples lie somewhat between the extremes of the eastern and western US in terms of the majority of components. There is a relatively even balance between sulphate and nitrate in the UK compared to the sulphate-rich situation in the eastern US and the nitrate-rich aerosol in the western US. The percentage of carbonaceous particles in the UK also lies somewhere between that of the eastern and western US. A comparison of the London and Birmingham data with measurements made at a site in Leeds in 1982 show that in terms of percentage composition, the most important change has been a substantial reduction in the sulphate content which is now very similar to that of nitrate. When mass concentrations are examined, it is clear that sulphate has reduced very substantially, as have carbonaceous particles, with other components having changed to a comparatively small extent. The reduction of 46% in the carbonaceous component of PM$_{2.5}$ over the approximately 20 years compares well with a reduction of 49% in the emissions of particulate matter from vehicle exhaust in the UK national inventories between 1982 and 2000.

Analysis of data from days with PM$_{10}$ in excess of 50$\mu gm^{-3}$ shows an approximate doubling of most components of the particles (with the exception of sodium chloride) relative to an average of samples from both high and pollution days. The most marked difference is a more than five-fold increase in fine particle nitrate concentrations such that nitrate salts represent almost a quarter of PM$_{10}$ mass on days in excess of 50$\mu gm^{-3}$ of PM$_{10}$. The data from roadside sites indicate a contribution of elevations in both secondary particle concentrations and traffic-generated carbonaceous particles and iron-rich dusts in contributing to elevated concentrations.

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References


