Particulate matter in the atmosphere: which particle properties are important for its effects on health?

Roy M. Harrison*, Jianxin Yin

*Division of Environmental Health and Risk Management, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Abstract

Whilst epidemiological studies have consistently demonstrated adverse effects of particulate matter exposure on human health, the mechanism of effect is currently unclear. One of the major issues is whether the toxicity of the particles resides in some particular fraction of the particles as defined by chemical composition or size. This article reviews selected data on the major and minor component composition of PM$_{2.5}$ and PM$_{10}$ particulate matter showing quite major geographic variations in composition which are not reflected in the exposure-response coefficients determined from the epidemiology which show remarkably little spatial variation. The issue of particle size is more difficult to address due to the scarcity of data. Overall, the data presented provides little support for the idea that any single major or trace component of the particulate matter is responsible for the adverse effects. The issue of particle size is currently unclear and more research is warranted.

Keywords: Airborne particulate matter; PM$_{10}$; Human health

1. Introduction

The London smog of December 1952 is estimated to have caused some 4000 excess deaths. The air pollutant concentrations judged against those of today in the same city were quite astronomic. Concentrations of black smoke exceeded 1600 $\mu$g m$^{-3}$ and of sulfur dioxide 700 ppb. The source of pollution was the burning of bituminous coal, mainly in domestic fireplaces, which is a source of both smoke and sulfur dioxide. Due to the very strong correlation of the two pollutants in all air pollution episodes at the time, there was little prospect of disentangling the effects of the two pollutants through epidemiological work, and the effects were ascribed to the mixture, with the World Health Organisation in its 1987 Air Quality Guidelines for Europe (WHO, 1987) setting a joint standard for black smoke exposure...

R.M. Harrison, J. Yin

and gravimetrically determined particulate matter) and sulfur dioxide, and the EU’s air quality Directive of 1980 setting a joint standard in which the permissible concentration of sulfur dioxide was dependent on the ambient concentration of smoke (Council of the European Communities, 1980).

It was not until the early 1990s that Schwartz et al. applied improved statistical methodologies and were able to demonstrate effects of particulate matter on health at concentrations hitherto believed safe, and demonstrated that such effects did not depend upon the presence of appreciable concentrations of sulfur dioxide (Department of Health, 1995). Much of the thinking regarding the toxicology of the smoke/sulfur dioxide mixture appears to have been based on the idea that the particulate matter acted as an agent to transfer sulfur dioxide on its surface to the deep lung, whereas in the absence of particles, most sulfur dioxide would be removed by uptake in the upper respiratory tract. The demonstration of effects of particles on their own necessitated a rethinking of the toxicology of a material which had previously been thought of as relatively innocuous except in the presence of SO₂. Indeed, in the early 1990s, whilst many informed workers were beginning to accept the results of the epidemiological studies, it was widely stated that there was no plausible mechanism of effect of particulate matter exposure. This view no doubt resulted from the absence of research, since at the time of writing this article the literature abounds with plausible mechanisms (see for example, Donaldson and MacNee, 1998).

Currently, there are, if anything, too many plausible mechanisms and too little established fact. This is not without its problems. In order to protect public health, governments and international organisations are quite rightly setting ambient air quality standards for particulate matter and are legislating for reductions in particle emissions from the key sectors. In both the USA and Europe these measures are in place and are set wholly in terms of the mass of particles. In considering the next steps, regulators are quite rightly posing the question of what property of particulate matter is responsible for the toxic effects and, therefore, whether a more cost-effective solution would be to regulate purely the toxic component rather than using the sledge hammer approach (which may prove very low on cost-effectiveness) of simply reducing mass emissions from all those sectors which are susceptible to control. Indeed, one worrying thought is that if techniques used to reduce the mass of particle emissions simply reduce the mean particle size and, therefore, have little influence on the number of particles, they may have little effect on health outcomes. The key questions would therefore appear to be: (a) what influence does chemical composition of particulate matter have on the magnitude of its effect; and (b) what is the influence of particle size on the ability of particles to induce toxic effects?

2. Particle chemistry

Perhaps the best research outcome, which could be hoped for, would be the identification of a given minor chemical component of particulate matter, which is solely responsible for adverse effects on health. However, the UK Department of Health Committee on the Medical Effects of Air Pollution (Department of Health, 1995) concluded that no known chemical substance is of sufficient toxicity given the current levels of exposure to particulate matter to explain the observed magnitude of health effects. Even the extremely toxic agents developed for chemical warfare would not have a sufficient level of toxicity. Epidemiological studies also argue against chemistry having an especially important influence. The greatest numbers of epidemiological studies have investigated the connection between total mortality and exposure to particulate matter measured as PM₁₀ (particles determined by mass passing an inlet with a 50% cut-off efficiency at a 10-μm aerodynamic diameter). There is a remarkable consistency between such studies irrespective of where they are carried out (Dockery and Pope, 1994; Lippmann, 1998) although a more recent review by the UK Department of Health (1998) did identify apparent modest differences between the results of US and European studies, but did not
offer a full explanation. Generally speaking, total daily mortality increases by approximately 1% per 10 μg m⁻³ increase in PM₁₀ concentration. Such findings appear to apply in both developed and developing countries where the pollutant mixes are expected to be rather different and seem to apply equally to the east and west of the USA where particulate matter composition is very different, with nitrates playing a major role on the west coast relative to sulfates and the opposite situation prevailing on the east coast (Lippmann, 1998).

On the other hand, it is difficult to imagine that chemical composition does not play a role. Chemical components of PM₁₀ are highly diverse. They range from near neutral and highly soluble substances such as ammonium sulfate, ammonium nitrate and sodium chloride through sooty particles made up largely of elemental carbon coated in organic compounds, and essentially insoluble minerals such as particles of clay. Some workers have expressed the view that it is almost inconceivable that the water-soluble components, which will rapidly dissolve in the well buffered lining fluids of the respiratory system, can exert any appreciable physiological effect. Yet, the soluble substances and thus by inference also the insoluble substances, represent widely differing fractions of the ambient aerosol in different locations, but no obvious differences in the coefficients of the epidemiological studies reflect this variation. One toxicological study has claimed to demonstrate that it is the soluble fraction which is responsible for pulmonary toxicity (Adamson et al., 1999). However, such a conclusion is based upon making aqueous extracts of airborne particles for laboratory experiments. This is experimentally demanding if the presence of ultrafine colloidal solids is to be wholly avoided, and the authors present no evidence to confirm that, for example, colloidal iron oxide particles have been wholly excluded.

Evidence is also being presented that trace metals influence the toxicity of airborne particulate matter. Such evidence derives from toxicological rather than epidemiological studies and depends mechanistically on the idea that metals are redox-active and can, therefore, induce or catalyse chemical change leading to production of free radicals such as the hydroxyl radical which have a known ability to cause tissue inflammation. Such findings are interesting, but as yet very far from conclusive. In the UK concentrations of most airborne metals have fallen dramatically in recent years and more rapidly than those of particulate matter as a whole (QUARG, 1993). Unfortunately, there seems to be no base of data from which to investigate whether health impacts have correlated with either trace metals or particle mass. However, in dealing with trace metals it must be recognised that a wide range of metals have been implicated and each has quite separate trends in concentration. The solubility and bioavailability of the metal will also be important, and this may have changed with time as the make-up of the particles has changed.

3. Particle size

The vast majority of epidemiological studies have used particle metrics such as PM₁₀, black smoke or sulfate concentration simply because these are the variables for which large datasets are available. There is a case for arguing that PM₂.₅ might better describe the component of particulate matter responsible for adverse effects since this smaller size fraction is capable of penetrating to the alveolar region of the respiratory system with far greater efficiency than the coarse particles of 2.5–10 μm aerodynamic diameter which make up the remaining part of PM₁₀. In the UK, and probably in many other countries, concentrations of PM₂.₅ and PM₁₀ are very highly correlated, (APEG, 1999) making the task of distinguishing between the two metrics in epidemiological studies almost impossible since the two do not behave as independent variables. However, studies from other parts of the world have sought to resolve whether it is PM₂.₅ or PM₁₀ which is the better metric, and do provide limited evidence that fine particles (PM₂.₅) are more toxic than coarse particles (PM₁₀–PM₂.₅) (Lippmann, 1998).

One of the more interesting findings from the toxicological studies is that ultrafine particles of less than 100 nm appear to have considerably
enhanced toxicity per unit mass and that their toxicity increases as particle size decreases (Donaldson and MacNee, 1998). This may be explained either through a greater surface area per unit mass if the toxic components reside solely or partially in the surface of the particles, or via the ability of ultrafine particles to penetrate the pulmonary interstitium. Seaton et al. (1995) have hypothesised that it is the ability of ultrafine particles to penetrate the lung wall inducing inflammation in the pulmonary interstitium, which in turn stimulates the production of clotting factors in the blood which is responsible for the recognised ability of airborne particles to exacerbate ischaemic heart disease, a health outcome which had previously been extremely hard to explain on mechanistic grounds.

Airborne particulate matter comprises particles of extremely diverse sizes. The smallest freshly formed particles are less than 5 nm in diameter and comprise only tens of molecules. Particles in the 3–50-nm range are highly abundant in urban air as a result of vehicle emissions. On the other hand, airborne particles can be as large as 100 μm, and even within the PM10 size range, a significant proportion of particle mass (but not number) may well be in the size range close to 10 μm. There are insufficient measurements of airborne particle size distributions to know how consistent size distributions are between cities in different parts of the world or how constant on a day-to-day basis. However, the data that are available on such measures as the PM2.5/PM10 ratio indicate that there can be quite appreciable differences dependent on the climate and sources of particles. Yet, the epidemiology based on total mortality does not show any obvious systematic geographic variation in the magnitude of effect per unit mass of particulate matter.

4. Factors which may influence the toxicity of airborne particulate matter

Properties expected to show geographic variation, which may influence particle toxicity, include the following:

1. bulk chemical composition;
2. trace element content;
3. strong acid content;
4. sulfate content; and
5. particle size distribution

These factors will now be considered in turn.

4.1. Bulk chemical composition

Airborne particulate matter may be considered as made up of major components, each representing several percent of the total mass of particles, together with trace element components usually representing less than 1% of total particle mass (Harrison and Jones, 1995). The term ‘bulk chemical composition’ refers to the relative abundance of the major components. Air samples from urban areas from around the world typically show the same major components, although in considerably different proportions according to the location of air sampling. These major components are typically the following:

1. Sulfate — derived predominantly from sulfur dioxide oxidation in the atmosphere. Because sulfur dioxide is oxidised only slowly, spatial gradients of sulfate on a scale of tens of miles are expected to be very small (Burton et al., 1996), over hundreds of miles they can be significant, and over entire continents, very large (QUARG, 1996). There may be a small local urban increment in sulfate (APEG, 1999).
2. Nitrate — this is formed mainly from the oxidation of atmospheric nitrogen dioxide, and one major form, ammonium nitrate, is believed to be in equilibrium in the atmosphere with its precursor gases ammonia and nitric acid vapour (Harrison and Msibi, 1994). In some environments, sodium nitrate predominates. Because nitrogen dioxide oxidises appreciably more rapidly than sulfur dioxide, and due to the sensitivity of ammonium nitrate concentrations to ambient ammonia concentrations which influence the dissociation, the spatial patterns of nitrate are ex-
pected to be considerably less uniform than those of sulfate.

3. Ammonium — when formed initially in the atmosphere, sulfate and nitrate are in the form of sulfuric and nitric acids. These are progressively neutralised by atmospheric ammonia forming ammonium salts (Harrison and Kitto, 1992). In most, but not all urban locations, the ammonium ion appreciably exceeds the hydrogen ion, which it displaces in the neutralisation process.

4. Chloride — the main sources of chloride are sea spray even at locations hundreds of miles from the coast, and during the winter months road de-icing salt. Chlorides also enter atmospheric particles as result of ammonia neutralisation of hydrochloric acid vapour, which is emitted, from sources such as incinerators and power stations.

5. Elemental carbon and organic carbon — combustion processes, nowadays most notably road traffic, emit sooty particles which contain carbon in the form of a core of solid black elemental carbon which often has a surface coating of semi-volatile organic compounds which condense from the exhaust gases (Amann and Siegla, 1982). Further organic carbon can be incorporated in the particles as a result of atmospheric photochemical processes which produce low volatility carbon compounds (Bowman et al., 1997).

6. Crustal materials — these include soil dusts and windblown rock-derived minerals. They are, therefore, quite diverse in composition reflecting local geology and surface conditions. Their concentration is dependent on climate as the processes which suspend them into the atmosphere tend to be favoured by dry surfaces and high winds. These particles reside mainly in the coarse particle fraction (Harrison et al., 1997a).

7. Biological materials — some studies have separately characterised material of biological origin which may include both small organisms such as bacteria as well as spores and pollens and fragments of cellulosic plant material (Matthias-Maser and Jaenicke, 1994). With the exception of some viruses, these are generally coarse in size, and in most studies have been characterised as organic carbon rather than separately as biological materials.

The bulk chemical composition of particulate matter can vary substantially between urban areas for a wide range of reasons. As indicated above, climatic factors strongly influence the concentrations of crustal material, and hence in dryer climates this component may be of greater relative importance. Sulfate particles depend on regional sulfur dioxide emissions and these can vary appreciably between countries and in different parts of a large country (see Table 1). The ammonia content of the air influences the ammonium concentration in the particles; since the major source of ammonia emissions is intensive agriculture, again spatial variability is to be expected. Variations within one large country are exemplified by the data in Fig. 1 showing typical compositions of PM\textsubscript{10}, PM\textsubscript{2.5}, and coarse particles in the eastern and western US. The most important differences lie in the PM\textsubscript{2.5} fraction with far lower sulfate concentrations and higher elemental and organic carbon concentrations in the western US than in the eastern US. Also in the eastern US, sulfate far exceeds nitrate, whilst in the western US, nitrate predominates. There are a number of reasons for this difference which relate to the relative importance of electricity generation from fossil fuels and road traffic as pollution sources (the former tends to emit sulfur dioxide, the latter predominantly nitrogen oxides) and the greater abundance of ammonia in the western US than the east, which tends to ‘fix’ the nitrate into the particles, whereas in the eastern US with low ammonia levels, ammonium nitrate is potentially unstable.

Data from Leeds, UK collected in 1982 (Fig. 2) and Birmingham, UK collected in 1995 (Fig. 3) show considerable similarity despite the passage of time. In the UK the sulfate-to-nitrate ratio by mass generally exceeds one, but does not approach the extremely high values seen in the eastern US. The UK, therefore, typically lies somewhere between the situation in the eastern and western USA with respect to sulfate and nitrate composition. The western US shows con-
Table 1
Bulk chemical composition (%) of particulate matter samples collected in different urban areas around the world

<table>
<thead>
<tr>
<th>Locations</th>
<th>Reference</th>
<th>Size (μm)</th>
<th>Total mass (μg m$^{-1}$)</th>
<th>EC</th>
<th>OC</th>
<th>Organic</th>
<th>TC</th>
<th>NO$_3$</th>
<th>SO$_4^{2-}$</th>
<th>NH$_4^+$</th>
<th>Cl$^-$</th>
<th>Crustal Minerals</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern US</td>
<td>USEPA (1996)</td>
<td>&lt; 10</td>
<td>–</td>
<td>3.3</td>
<td>6.1</td>
<td>8.5</td>
<td>9.4</td>
<td>1.2</td>
<td>27.8</td>
<td>10.7</td>
<td>–</td>
<td>–</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5–10</td>
<td>–</td>
<td>3.9</td>
<td>14.9</td>
<td>20.9</td>
<td>18.8</td>
<td>1.1</td>
<td>34.1</td>
<td>13.0</td>
<td>–</td>
<td>–</td>
<td>4.3</td>
</tr>
<tr>
<td>Western US</td>
<td>USEPA, (1996)</td>
<td>&lt; 10</td>
<td>–</td>
<td>5.1</td>
<td>21.4</td>
<td>30.0</td>
<td>26.5</td>
<td>24.0</td>
<td>4.6</td>
<td>6.7</td>
<td>–</td>
<td>–</td>
<td>36.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5–10</td>
<td>–</td>
<td>5.0</td>
<td>22.8</td>
<td>38.9</td>
<td>42.5</td>
<td>15.7</td>
<td>10.8</td>
<td>7.5</td>
<td>–</td>
<td>–</td>
<td>14.6</td>
</tr>
<tr>
<td>South-west US</td>
<td>Vasconcelos et al. (1994)</td>
<td>&lt; 2.5</td>
<td>–</td>
<td>3.4</td>
<td>6.1</td>
<td>9.4</td>
<td>1.2</td>
<td>27.8</td>
<td>10.7</td>
<td>3.1</td>
<td>0.8</td>
<td>–</td>
<td>69.3</td>
</tr>
<tr>
<td>Southern California</td>
<td>Chow et al. (1994)</td>
<td>&lt; 10</td>
<td>–</td>
<td>7.1</td>
<td>3.5</td>
<td>20.0</td>
<td>12.7</td>
<td>13.2</td>
<td>5.7</td>
<td>18.2</td>
<td>–</td>
<td>–</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 2.5</td>
<td>–</td>
<td>3.7</td>
<td>5.0</td>
<td>26.5</td>
<td>9.8</td>
<td>20.9</td>
<td>9.0</td>
<td>0.4</td>
<td>2.5</td>
<td>–</td>
<td>23.9</td>
</tr>
<tr>
<td>Edison, California</td>
<td>Chow et al. (1996)</td>
<td>&lt; 10</td>
<td>–</td>
<td>52.5</td>
<td>5.7</td>
<td>19.7</td>
<td>27.6</td>
<td>25.4</td>
<td>6.3</td>
<td>2.0</td>
<td>–</td>
<td>46.1</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 2.5</td>
<td>–</td>
<td>49.6</td>
<td>6.0</td>
<td>31.4</td>
<td>44.0</td>
<td>37.4</td>
<td>6.0</td>
<td>3.0</td>
<td>2.0</td>
<td>–</td>
<td>35.0</td>
</tr>
<tr>
<td>Los Angeles</td>
<td>Kao and Friedlander (1994)</td>
<td>&lt; 15</td>
<td>–</td>
<td>74.3</td>
<td>7.5</td>
<td>8.2</td>
<td>15.7</td>
<td>10.8</td>
<td>8.3</td>
<td>5.0</td>
<td>–</td>
<td>–</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 2.5</td>
<td>–</td>
<td>35.5</td>
<td>–</td>
<td>–</td>
<td>33.8</td>
<td>7.9</td>
<td>19.2</td>
<td>6.8</td>
<td>4.2</td>
<td>–</td>
<td>28.1</td>
</tr>
<tr>
<td>Leeds, UK</td>
<td>Clarke et al. (1984)</td>
<td>2.5–15</td>
<td>&lt; 10</td>
<td>22.2</td>
<td>–</td>
<td>–</td>
<td>50.0</td>
<td>6.6</td>
<td>26.1</td>
<td>9.8</td>
<td>1.8</td>
<td>–</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5–15</td>
<td>13.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>13.3</td>
<td>5.8</td>
<td>7.4</td>
<td>2.5</td>
<td>8.2</td>
<td>–</td>
<td>62.8</td>
</tr>
<tr>
<td>Birmingham, UK</td>
<td>Harrison et al. (1997)</td>
<td>&lt; 10</td>
<td>10.0</td>
<td>25.7</td>
<td>18.0</td>
<td>20.0</td>
<td>38.0</td>
<td>6.0</td>
<td>17.0</td>
<td>6.0</td>
<td>2.0</td>
<td>–</td>
<td>31.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5–15</td>
<td>18.9</td>
<td>–</td>
<td>21.0</td>
<td>–</td>
<td>3.0</td>
<td>6.0</td>
<td>18.0</td>
<td>22.0</td>
<td>–</td>
<td>–</td>
<td>20.0</td>
</tr>
<tr>
<td>Brisbane, Australia</td>
<td>Chan et al. (1997)</td>
<td>&lt; 2.5</td>
<td>7.3</td>
<td>19.3</td>
<td>–</td>
<td>–</td>
<td>27.0</td>
<td>2.6</td>
<td>5.0</td>
<td>10.0</td>
<td>9.7</td>
<td>6.1</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5–10</td>
<td>10.4</td>
<td>2.8</td>
<td>–</td>
<td>13.0</td>
<td>4.3</td>
<td>1.4</td>
<td>2.7</td>
<td>22.0</td>
<td>29.0</td>
<td>–</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5–10</td>
<td>28.1</td>
<td>13.9</td>
<td>8.8</td>
<td>14.4</td>
<td>3.3</td>
<td>2.3</td>
<td>6.1</td>
<td>–</td>
<td>–</td>
<td>6.1</td>
<td>14.0</td>
</tr>
<tr>
<td>Lahore, Pakistan</td>
<td>Smith et al. (1996)</td>
<td>TSP</td>
<td>607</td>
<td>2.9</td>
<td>13.1</td>
<td>–</td>
<td>16.0</td>
<td>2.1</td>
<td>3.0</td>
<td>1.2</td>
<td>–</td>
<td>–</td>
<td>16.4</td>
</tr>
<tr>
<td>Hong Kong</td>
<td>Qin et al. (1997)</td>
<td>RSP</td>
<td>66.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>57.1</td>
<td>2.8</td>
<td>14.4</td>
<td>3.3</td>
<td>2.3</td>
<td>–</td>
<td>6.1</td>
</tr>
<tr>
<td>Antwerp, Belgium</td>
<td>Van Borm et al. (1989)</td>
<td>0.2–15</td>
<td>18.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>21.3</td>
<td>–</td>
<td>18.9</td>
<td>3.2</td>
<td>–</td>
<td>30.0</td>
<td>26.6</td>
</tr>
</tbody>
</table>

$^a$Note. (1) TC = EC + OC; ‘-’ means not measured.

$^b$Indicates reconstructed.
Fig. 1. Comparison of typical major component composition of airborne particulate matter from the eastern and western USA (USEPA, 1996).

siderably more organic and elemental carbon than the eastern US with concentrations in Leeds and Birmingham more similar to the western US.

Published data for other cities such as Sapporo (Japan) (Kaneyasu et al., 1995), Antwerp (Belgium) (Van Borm et al., 1989) and Brisbane (Australia) (Chan et al., 1997) are available and fit broadly within the range exemplified by the eastern and western USA, although in Brisbane the contribution of seasalt is appreciable (12.6% of PM$_{10}$).

4.2. Trace element content

It has long been recognised that some trace metals such as lead, cadmium and mercury are highly toxic in sizeable doses, but exposures through inhalation of urban airborne particulate matter in the developed world are likely to be wholly insufficient to cause toxic effects through classical mechanisms of toxicity (Department of Health, 1995). However, some recently published work has suggested that transition metals, and particularly iron, may have adverse effects through non-classical mechanisms such as contributing to the production of hydroxyl radicals through the Fenton reaction (Gilmour et al., 1996).

Since concentrations of trace metals in the atmospheres of most cities in the developed world have declined sharply in response to pollution control measures in recent years, rather little attention is now given to their measurement. With the exception of metals such as lead, whose predominant source in many countries is still from road traffic leading to wide dispersal in city air, other trace metals which arise predominantly from industrial sources are less spatially uniform and hence data are very sensitive to the precise location of measurements. However, as Tables 2 and 3 demonstrate, reported concentrations of trace metals in major cities do not vary immensely between the cities. An important point to note regarding the majority of these trace metals is that their chemical speciation, and hence bioavailability and potential to participate in specific chemical reactions such as the Fenton reaction,
varies significantly according to their source, hence, simple measurements of the total airborne concentrations of a metal may not be representative of its potential to participate in processes deleterious to health.

4.3. Strong acid content

As noted earlier, when nitrate and sulfate are formed in the atmosphere from oxidation of nitrogen dioxide and sulfur dioxide, respectively, they are formed as their strong acids, nitric acid and sulfuric acid. Nitric acid is a vapour which can only incorporate into airborne particles to any significant degree by loss of its acidity either through displacing hydrochloric acid from seasalt particles to form sodium nitrate, or by ammonia neutralisation to form ammonium nitrate (Harrison and Allen, 1990). In the case of sulfuric acid, however, the acid is involatile, and once formed, is immediately incorporated into airborne particles which are only subsequently neutralised by atmospheric ammonia. Thus, in environments with low airborne ammonia concentrations, airborne particles may have an appreciable strong acid content reflecting wholly or partially unneutralised sulfuric acid. This is relatively difficult to measure and there have been only a very limited number of reports of its concentration in the atmosphere. No recent review of these data is available, but Kitto and Harrison (1992), reviewing data published in North America and Europe over the period 1978–1991, (which is not necessarily representative of the 1990s), found large geographic variations in the range of measurements. The same is reflected in US data reported in USEPA (1996).

One major difference between the eastern and western US which is not clearly exemplified by Fig. 1 is that airborne particles in the western US tend to be relatively neutral due to ample ammonia availability (USEPA, 1996), whereas in the eastern US ammonia concentrations are far lower and appreciable atmospheric acidity can be observed. Lippmann (1989) has argued forcibly that it is the strong acid content of airborne particles which is responsible for their toxic action. Were this to be the case, one would expect to see considerable differences between exposure-response functions for PM$_{10}$ from the eastern and western US and between the eastern US and countries such as the UK, where at inland locations particulate matter tends to be well neutralised.

4.4. Sulfate content

Two cross-sectional studies, the Harvard Six
Cities study (Dockery et al., 1993) and the American Cancer Society study (Pope et al., 1995) have related mortality rates to airborne concentrations of sulfate showing a strong correlation. Additionally, some time series studies have used sulfate as a surrogate for fine particulate matter (Ostro, 1990). Schwartz et al. (1996) have also carried out time series studies of daily mortality in relation to PM$_{10}$, PM$_{2.5}$, and sulfate in each or the six cities, finding a stronger association for PM$_{2.5}$ than for sulfate, and it appears that as it is a major component of PM$_{2.5}$, sulfate may be acting as a surrogate for the entire fine particle mass or for some other specific component. As may be seen from the earlier discussion on the bulk chemical composition of airborne particulate matter, the sulfate content of particles is highly variable from city-to-city. A study in Philadelphia (Burton et al., 1996) showed 48% of PM$_{10}$ to comprise sulfate-related fine particles, whereas in Rubidoux, California, sulfate comprised only 6.2% of PM$_{10}$ (Chow et al., 1992). Whilst, if sulfate represents a relatively constant proportion of PM$_{10}$, it might act as a surrogate in a time series study, if its relative abundance varies between locations then differences in the PM$_{10}$-health outcome coefficients for different locations would be expected.

4.5. Particle size distribution

The work of Schwartz et al. (1996) has demonstrated a strong relationship between PM$_{2.5}$ and mortality in six cities based on time series studies and shown little, if any, relationship with coarse particles in the 2.5–10-μm size range. Additionally, the mechanistic work of Oberdörster, Donaldson and others (e.g. Oberdörster et al., 1995) has attached special importance to ultrafine particles (usually defined as less than 100 nm), or even those less than 50 nm diameter. Thus, the size distribution of airborne particles may have an important consequence for the health impacts.

Friedlander (1977) has introduced the concept of the ‘self-preserving aerosol size distribution’. This concept argues that over typical atmospheric timescales airborne particulate matter will tend...
Table 2: Comparison of average urban concentrations for trace metals at different locations in the USA (data from USEPA, 1996)

<table>
<thead>
<tr>
<th>Species</th>
<th>Boston</th>
<th>Phoenix</th>
<th>Los Angeles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Fine</td>
<td>Coarse</td>
</tr>
<tr>
<td></td>
<td>&lt; 10 µm</td>
<td>&lt; 2.5 µm</td>
<td>2.5 – 10 µm</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>629</td>
<td>98</td>
<td>533</td>
</tr>
<tr>
<td>Ca</td>
<td>1139</td>
<td>70</td>
<td>1069</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sc</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Be</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sb</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>3458</td>
<td>-</td>
<td>3458</td>
</tr>
<tr>
<td>Ti</td>
<td>154</td>
<td>-</td>
<td>154</td>
</tr>
<tr>
<td>V</td>
<td>28</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>Cr</td>
<td>8</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Mn</td>
<td>30</td>
<td>1</td>
<td>29</td>
</tr>
<tr>
<td>Fe</td>
<td>1733</td>
<td>121</td>
<td>1612</td>
</tr>
<tr>
<td>Ni</td>
<td>34</td>
<td>12</td>
<td>22</td>
</tr>
<tr>
<td>Cu</td>
<td>58</td>
<td>35</td>
<td>23</td>
</tr>
<tr>
<td>Zn</td>
<td>100</td>
<td>46</td>
<td>54</td>
</tr>
<tr>
<td>As</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Se</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>462</td>
<td>285</td>
<td>177</td>
</tr>
<tr>
<td>Si</td>
<td>6904</td>
<td>144</td>
<td>6760</td>
</tr>
<tr>
<td>Ba</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rb</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>In</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total mass</td>
<td>140 400</td>
<td>34 800</td>
<td>105 600</td>
</tr>
</tbody>
</table>
Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>Chicago</th>
<th>Houston</th>
<th>St. Louis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Fine</td>
<td>Coarse</td>
</tr>
<tr>
<td></td>
<td>&lt; 10 μm</td>
<td>&lt; 2.5 μm</td>
<td>2.5 – 10 μm</td>
</tr>
<tr>
<td>Na</td>
<td>22</td>
<td>22</td>
<td>17</td>
</tr>
<tr>
<td>K</td>
<td>161</td>
<td>61</td>
<td>101</td>
</tr>
<tr>
<td>Ca</td>
<td>761</td>
<td>45</td>
<td>716</td>
</tr>
<tr>
<td>Mg</td>
<td>118</td>
<td>12</td>
<td>106</td>
</tr>
<tr>
<td>Sc</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Be</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 41</td>
<td>&lt; 29</td>
<td>&lt; 12</td>
</tr>
<tr>
<td>Sb</td>
<td>&lt; 59</td>
<td>&lt; 42</td>
<td>&lt; 17</td>
</tr>
<tr>
<td>Al</td>
<td>269</td>
<td>46</td>
<td>223</td>
</tr>
<tr>
<td>Ti</td>
<td>19</td>
<td>29</td>
<td>19</td>
</tr>
<tr>
<td>V</td>
<td>&lt; 13</td>
<td>&lt; 9</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 7.3</td>
<td>&lt; 5</td>
<td>&lt; 2.4</td>
</tr>
<tr>
<td>Mn</td>
<td>13</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Fe</td>
<td>432</td>
<td>89</td>
<td>344</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 1.8</td>
<td>&lt; 1</td>
<td>&lt; 0.7</td>
</tr>
<tr>
<td>Cu</td>
<td>17</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>90</td>
<td>52</td>
<td>38</td>
</tr>
<tr>
<td>As</td>
<td>&lt; 4.3</td>
<td>&lt; 3</td>
<td>&lt; 1.3</td>
</tr>
<tr>
<td>Se</td>
<td>&lt; 1.7</td>
<td>&lt; 1</td>
<td>&lt; 0.6</td>
</tr>
<tr>
<td>Sr</td>
<td>–</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Pb</td>
<td>32</td>
<td>27</td>
<td>5</td>
</tr>
<tr>
<td>Si</td>
<td>831</td>
<td>74</td>
<td>739</td>
</tr>
<tr>
<td>Ba</td>
<td>&lt; 130</td>
<td>&lt; 91</td>
<td>38</td>
</tr>
<tr>
<td>Hg</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rb</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pd</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ag</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>In</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 70</td>
<td>&lt; 49</td>
<td>&lt; 21</td>
</tr>
<tr>
<td>La</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total mass</td>
<td>28 540</td>
<td>13 570</td>
<td>14 970</td>
</tr>
</tbody>
</table>

*Note: (a) Sampling sites: (1) Boston, eastern US (1980); (2) Phoenix, western US (13/10/1989–17/1/1990); (3) Los Angeles, western US (Summer, 1987); (4) Chicago, Central US (7/1994); (5) Houston, Central US (10–19/9/1980); (6) St. Louis, Central US (8–9/1976); and (b) ‘-’ means not measured.
towards a rather constant distribution of sizes as very small particles are lost by coagulation with larger particles, and very large particles deposit from the atmosphere by gravitational and other mechanisms. This concept provides a sound understanding of the behaviour of aerosols on time scales of days, but many of the processes involved are too slow to influence the aerosol size distribution substantially on urban scales. Thus, differences in particle size distributions are to be expected between and within urban areas, but currently insufficient data are available to allow full quantification of this effect. However, data from Birmingham, UK show considerable seasonal influence on the proportion of coarse particles (2.5–10 µm) in PM$_{10}$, ranging from approximately 20% in the winter to 50% in the summer months (Harrison et al., 1997a). Looking at data from across the USA, PM$_{2.5}$ and PM$_{10}$ show a highly variable relationship, with some daily data showing in excess of 90% coarse particles whilst at other sites on other days the percentage of coarse particles is only approximately 10%. Based on the work of Schwartz et al. (1996) relationships based on PM$_{2.5}$ are far more likely to be transferable than those based on PM$_{10}$, especially in

| Species | Birmingham UK$^1$ | Coimbra$^2$ | Lahore$^3$ | Wageningen$^4$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine</td>
<td>Coarse</td>
<td>Total</td>
<td>Fine</td>
</tr>
<tr>
<td></td>
<td>&lt; 2.1 µm (ng m$^{-3}$)</td>
<td>2.1 – 10 µm (ng m$^{-3}$)</td>
<td>&lt; 10 µm (ng m$^{-3}$)</td>
<td>&lt; 0.95 µm (ng m$^{-3}$)</td>
</tr>
<tr>
<td>Na</td>
<td>348</td>
<td>698</td>
<td>1050</td>
<td>360</td>
</tr>
<tr>
<td>K</td>
<td>127</td>
<td>71.5</td>
<td>199</td>
<td>320</td>
</tr>
<tr>
<td>Ca</td>
<td>40</td>
<td>168</td>
<td>208</td>
<td>520</td>
</tr>
<tr>
<td>Mg</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sc</td>
<td>4.6</td>
<td>8.1</td>
<td>12.7</td>
<td>–</td>
</tr>
<tr>
<td>Be</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cd</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.5</td>
</tr>
<tr>
<td>Sb</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
</tr>
<tr>
<td>Al</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>840</td>
</tr>
<tr>
<td>Ti</td>
<td>4.7</td>
<td>11.9</td>
<td>16.6</td>
<td>–</td>
</tr>
<tr>
<td>V</td>
<td>5.0</td>
<td>2.4</td>
<td>7.4</td>
<td>12.1</td>
</tr>
<tr>
<td>Cr</td>
<td>6.4</td>
<td>6.2</td>
<td>12.6</td>
<td>19.9</td>
</tr>
<tr>
<td>Mn</td>
<td>9.9</td>
<td>6.4</td>
<td>16.3</td>
<td>13.5</td>
</tr>
<tr>
<td>Fe</td>
<td>114.</td>
<td>187.</td>
<td>301.</td>
<td>190.</td>
</tr>
<tr>
<td>Ni</td>
<td>2.9</td>
<td>1.9</td>
<td>4.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Cu</td>
<td>30.2</td>
<td>8.5</td>
<td>38.7</td>
<td>22.4</td>
</tr>
<tr>
<td>Zn</td>
<td>297</td>
<td>55.6</td>
<td>353.</td>
<td>50.</td>
</tr>
<tr>
<td>As</td>
<td>4.2</td>
<td>1.5</td>
<td>5.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Se</td>
<td>2</td>
<td>1.1</td>
<td>3.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Sr</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pb</td>
<td>73.9</td>
<td>17.1</td>
<td>91</td>
<td>250</td>
</tr>
<tr>
<td>Si</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ba</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hg</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rb</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pd</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ag</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>In</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sn</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>La</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total mass</td>
<td>–</td>
<td>–</td>
<td>47000</td>
<td>28600</td>
</tr>
</tbody>
</table>
relation to cities with widely varying proportions of coarse particle mass.

There are far fewer data from which to make any judgement on the proportion of ultrafine particles in the atmosphere. Such particles are better represented by measurements of particle number which respond very largely to particles less than 100 nm in diameter which dominate the number count, rather than of mass of particles below a given size threshold, such as 100 nm. The data which are available suggest that ultrafine particle numbers are very responsive to local sources and thus measurements close to combustion sources can show concentrations orders of magnitude above the local background. This local small scale variability makes any assessment of

---

### Table 3 (Continued)

| Species | Arnhem<sup>a</sup> | | Anaheim<sup>a</sup> | | Azusa<sup>b</sup> | | Edison<sup>c</sup> |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|
|         | Total < 10 μm (ng m<sup>-3</sup>) | Fine < 2.5 μm (ng m<sup>-3</sup>) | Total < 10 μm (ng m<sup>-3</sup>) | Fine < 2.5 μm (ng m<sup>-3</sup>) | Total < 10 μm (ng m<sup>-3</sup>) | Fine < 2.5 μm (ng m<sup>-3</sup>) | Total < 10 μm (ng m<sup>-3</sup>) | Fine < 2.5 μm (ng m<sup>-3</sup>) |
| Na      | 327.5         | 59             | 1659.3         | 231.8          | 1541.8         | 193.4          | 1378           | 1186           |
| K       | 268.5         | 88             | 278.7          | 92.9           | 617.9          | 111.3          | 1204           | 1043           |
| Ca      | 491           | 8.4            | 1304.7         | 150.4          | 1204           | 55.4           | 1204           | 1043           |
| Mg      | 348.8         | 36             | 604.5          | 55.4           |                |                |                |                |
| Be      | 90            | 11.5           | 1378           | 1186           |                |                |                |                |
| Cd      | 3          | 4              |                |                |                |                |                |                |
| Sb      | 9            | 6              |                |                |                |                |                |                |
| Al      | 701.2         | 35.1           | 2270.5         | 184.7          | 2684           | 1824           |                |                |
| Ti      | 59.9          | 3.6            | 251            | 29.9           | 173            | 151            |                |                |
| V       | 5.1           | 5.6            | 7.5            | 5.7            | 3              | 3              |                |                |
| Cr      | 19.6          | 18.5           | 19.6           | 18             | 1              | 0              |                |                |
| Mn      | 23.6          | 12.2           | 79.2           | 15.7           | 36             | 33             |                |                |
| Fe      | 598.9         | 29.6           | 1840.9         | 281.9          | 2140           | 1953           |                |                |
| Ni      | 4.7           | 4.5            | 4.6            | 4.5            | 4              | 3              |                |                |
| Cu      | 10.3          | 39.6           | 13.6           | 13.4           | 11             | 10             |                |                |
| Zn      | 24.8          | 33.3           | 168            | 55.3           | 28             | 25             |                |                |
| As      | 7             | 12.1           | 7.3            | 18.1           | 2              | 2              |                |                |
| Se      | 8.4           | 11.5           | 8.7            | 11.5           | 1              | 1              |                |                |
| Sr      | 18.7          | 17.6           | 18.4           | 19.2           | 13             | 11             |                |                |
| Pb      | 50.4          | 34.6           | 81.1           | 48.6           | 10             | 9              |                |                |
| Si      | 1922.8        | 33.8           | 5721.3         | 482.9          | 6708           | 5020           |                |                |
| Ba      | 42            | 7.5            | 137.5          | 26.5           | 68             | 70             |                |                |
| Hg      | 20.2          | 20.4           | 21.1           | 19.8           |                |                |                |                |
| Rb      | 5             | 4              |                |                |                |                |                |                |
| Zr      | 3             | 3              |                |                |                |                |                |                |
| Pd      | 5             | 6              |                |                |                |                |                |                |
| Ag      | 8             | 6              |                |                |                |                |                |                |
| In      | 6             | 4              |                |                |                |                |                |                |
| Sn      | 9             | 10             |                |                |                |                |                |                |
| La      | 23            | 21             |                |                |                |                |                |                |
| Total mass | 68150         | 38950          | 51300          | 26800          | 92100          | 47100          | 52464          | 49647          |

---

<sup>a</sup>Note. (a) Reference: 1, Smith (1995); 2, Harrison et al. (1997b); 3, Smith et al. (1996); 4 and 5, Janssen et al. (1997); 6 and 7, Chow et al. (1994); 8, Chow et al. (1996). (b) Sampling sites: 1 Birmingham University campus, UK (2/92 and 8/92); 2 Santa Cruz Church, Coimbra, Beira Litoral, Portugal (3/92); 3 University of Engineering and Technology, Lahore, Pakistan (3/92); 4 and 5, 11 day sampling (19/6/87–3/9/87) at Anaheim and Azusa, Southern California, USA; 8 Edison, Central California, USA (13/7–24/8, 1990); (c) ‘-‘ means not measured.
Table 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Central Birmingham</th>
<th>Ward End</th>
<th>Hodge Hill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle count (1000 s particles cm$^{-3}$)</td>
<td>36.6</td>
<td>28.6</td>
<td>96</td>
</tr>
<tr>
<td>Mean PM10 (µg m$^{-3}$)</td>
<td>23.6</td>
<td>23.5</td>
<td>PM$_{10}^\cdot$ 20.0</td>
</tr>
<tr>
<td>PM/particle count (slope from regression line, ×10$^{-11}$ g particle$^{-1}$)</td>
<td>0.4</td>
<td>0.38–0.46</td>
<td>PM$_{10}^\cdot$ 0.08</td>
</tr>
<tr>
<td>PM/particle count (slope from regression line, ×10$^{-13}$ g particle$^{-1}$)</td>
<td>0.35</td>
<td>0.3–0.37</td>
<td>PM$_{2.5}^\cdot$ 0.08</td>
</tr>
<tr>
<td>Reciprocal of slope (×10$^{10}$ particles µg$^{-1}$) hourly values</td>
<td>2.5</td>
<td>2.2–2.6</td>
<td>PM$_{10}^\cdot$ 12.5</td>
</tr>
<tr>
<td>Reciprocal of slope (×10$^{10}$ particles µg$^{-1}$) daily values</td>
<td>2.0</td>
<td>2.7–3.3</td>
<td>PM$_{2.5}^\cdot$ 14.3</td>
</tr>
</tbody>
</table>

a Note. Data are aggregates of more than one sampling period at each site.
b Sites are influenced by local traffic, Hodge Hill > Central Birmingham > Ward End.

differences between cities extremely difficult. However, a well selected background site would probably represent background ultrafine particle concentrations across a considerable area, and work in Birmingham has shown a rather good correlation between daily particle count and PM$_{10}$ mass for such a site (QUARG, 1996; Harrison et al., 1999). However, at hotspot locations strongly influenced by local traffic or other sources, such correlations are unlikely to be found. At present the data are so limited that it is not possible to say whether ultrafine particle number or total particle count (as surrogate) shows a similar numerical ratio to PM$_{10}$ in all cities. Indeed, within Birmingham even background sites showed some variability in the ratio (see Table 4) and the more traffic-influenced Hodge Hill site showed a much different ratio to the better located background locations. Results of other studies in which particle number counts have been reported are summarised in Table 5.

5. Conclusions

In general there are strong similarities between airborne particulate matter sampled in cities in developed countries across the world. The same bulk chemical components are present as well as trace elements at broadly comparable concentration levels. In some less developed countries, however, the situation is very different due to high pollutant loadings and much wind-blown coarse dust (Harrison et al., 1997b). Strong acid and sulfate contents can vary appreciably between locations. As a typical range it is clear that when expressed as a percentage of PM$_{10}$ mass, any of the components described could readily vary by one order of magnitude between cities with differing pollution climates. In this context the apparent similarity of exposure-response functions from cities around the world is surprising.

If the crucial factor relates to the particle size distribution, the data are far more sparse and conclusions are more difficult to draw. Whilst systematic variations undoubtedly exist between the PM$_{2.5}$/PM$_{10}$ ratios for different cities, over a period of a year these are likely to be of the order of two or three at most between cities and unlikely to be as great as an order of magnitude for cities in the developed world. If it is ultrafine particle number or mass which is the critical factor, the data are currently far too few to draw any conclusions whatever regarding relationships between cities. Local spatial variability is also likely to be so great in relation to ultrafine parti-
Table 5
Measurements of particle number count in urban areas

<table>
<thead>
<tr>
<th>Location</th>
<th>Nature of site</th>
<th>Sampling period</th>
<th>Instrument</th>
<th>Particle count and mass</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birmingham</td>
<td>Urban centre</td>
<td>13/9/94 – 23/10/94</td>
<td>TSI, 3025 CNC &amp; TEOM</td>
<td>Mean particle count: $3.7 \times 10^4$ cm$^{-3}$</td>
<td>Harrison et al. (1999)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean PM$_{10}$: 23.6 µg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>9–11/1995</td>
<td>TSI, 3022 CNC &amp; TEOM</td>
<td>Mean particle count: $2.9 \times 10^4$ cm$^{-3}$</td>
<td>Harrison et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>background</td>
<td></td>
<td>CNC &amp; TEOM</td>
<td>Mean PM$_{10}$: 23.5 µg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean PM$_{2.5}$: 20.0 µg m$^{-3}$</td>
<td>Harrison et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>22/11/96 – 2/12/97</td>
<td>TSI, 3071</td>
<td>Mean particle count: 1.6–1.9 × 10$^4$ cm$^{-3}$</td>
<td>Shi et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>Roadside</td>
<td></td>
<td></td>
<td>Mean PM$_{2.5}$: 40.6 µg m</td>
<td>Hughes et al. (1998)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DMPS/CPC 3022</td>
<td>Mean particle count: $1.3 \times 10^5$ cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DMA/CNC3760</td>
<td>±8.9 × 10$^3$</td>
<td>Tuch et al. (1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DEMA &amp; OPC</td>
<td>Mean particle count: 1.8 × 10$^5$ cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean PM$_{2.5}$: 34.02–25.52 µg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean PM$_{2.5}$: 73.8 µg m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>*Mean PM$_{2.5}$: 46.6 µg m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Daily mean particle count: 2 × 10$^4$ – 8 × 10$^4$ cm$^{-3}$</td>
<td>Buzorius et al. (1999)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Particle count range: 5 × 10$^4$ – 7 × 10$^4$ cm$^{-3}$</td>
<td>Morawska et al., (1999)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
cible to PM$_{10}$ relationships that any assessment will be experimentally difficult to conduct.

References


Chan YC, Simpson RW, Vowles PD, Cohen DD, Bailey GM. Characterisation of chemical species in PM$_{2.5}$ and PM$_{10}$ aerosols in Brisbane, Australia. Atmos Environ 1997;31:3773–3785.


Harrison RM, Deacon AR, Jones MR, Appleby RS. Sources and processes affecting concentrations of PM$_{10}$ and PM$_{2.5}$ in Birmingham, UK. Atmos Environ 1997a;31:4103–4117.


Lippmann M. The 1997 US EPA standards for particulate matter and ozone, In Issues in Environmental Science and


Tuch TH, Brand P, Wichmann HE, Heyder J. Variation of particle number and mass concentration in various size ranges of ambient aerosols in eastern Germany. Atmos Environ 1997;31:4193–4197.


