



ELSEVIER

The Science of the Total Environment 249 (2000) 85–101

**the Science of the  
Total Environment**

An International Journal for Scientific Research  
Into the Environment and its Relationship with Man

www.elsevier.com/locate/scitotenv

# 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. © 2000 Elsevier Science B.V. All rights reserved.

*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 astronomical. Concentrations of black smoke ex-

ceeded  $1600 \mu\text{g m}^{-3}$  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

\* Corresponding author. Tel.: +44-121-414-3494; fax: +44-121-414-3709.

E-mail address: r.m.harrison.ipe@bham.ac.uk (R.M. Harrison)

(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 SO<sub>2</sub>. 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 PM<sub>10</sub> (particles determined by mass passing an inlet with a 50% cut-off efficiency at a 10- $\mu$ m 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  $10 \mu\text{g m}^{-3}$  increase in  $\text{PM}_{10}$  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  $\text{PM}_{10}$  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 catal-

yse 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  $\text{PM}_{10}$ , black smoke or sulfate concentration simply because these are the variables for which large datasets are available. There is a case for arguing that  $\text{PM}_{2.5}$  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  $\mu\text{m}$  aerodynamic diameter which make up the remaining part of  $\text{PM}_{10}$ . In the UK, and probably in many other countries, concentrations of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  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  $\text{PM}_{2.5}$  or  $\text{PM}_{10}$  which is the better metric, and do provide limited evidence that fine particles ( $\text{PM}_{2.5}$ ) are more toxic than coarse particles ( $\text{PM}_{10}-\text{PM}_{2.5}$ ) (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  $\mu\text{m}$ , and even within the  $\text{PM}_{10}$  size range, a significant proportion of particle mass (but not number) may well be in the size range close to 10  $\mu\text{m}$ . 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  $\text{PM}_{2.5}/\text{PM}_{10}$  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 Sieglä, 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  $PM_{10}$ ,  $PM_{2.5}$  and coarse particles in the eastern and western US. The most important differences lie in the  $PM_{2.5}$  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<sup>a</sup>

Locations	Reference	Size ( $\mu\text{m}$ )	Total mass ( $\mu\text{g m}^{-3}$ )	EC	OC	Organic	TC	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{Cl}^-$	Crustal	Minerals	Other
Eastern US	USEPA (1996)	< 10	–	3.3	6.1	8.5	9.4	1.2	27.8	10.7	–	–	19.6	28.9
		< 2.5	–	3.9	14.9	20.9	18.8	1.1	34.1	13.0	–	–	4.3	22.8
		2.5–10	–	–	–	–	–	–	4.9	1.8	–	–	51.8	41.5
Western US	USEPA, (1996)	< 10	–	5.1	21.4	30.0	26.5	24.0	4.6	6.7	–	–	36.3	0.0
		< 2.5	–	14.7	27.8	38.9	42.5	15.7	10.8	7.5	–	–	14.6	0.0
		2.5–10	–	–	–	–	–	–	3.1	0.8	–	–	69.3	26.8
South-west US <sup>b</sup>	Vasconcelos et al. (1994)	< 2.5	3.4	–	–	–	29.3	–	13.3	26.7	–	24.0	–	6.7
		2.5–15	4.8	–	–	–	–	–	1.3	2.5	–	88.5	–	7.7
Southern California (urban) <sup>b</sup>	Chow et al. (1994)	< 10	71.7	3.5	–	20.0	–	12.7	13.2	5.7	1.3	18.2	–	19.3
		< 2.5	37.0	5.0	–	26.5	–	9.8	20.9	9.0	0.4	2.5	–	23.9
Edison, California <sup>b</sup>	Chow et al. (1996)	< 10	52.5	5.7	19.7	27.6	25.4	3.0	6.3	2.0	–	46.1	–	4.3
Los Angeles <sup>b</sup>	Kao and Friedlander (1994)	< 2.5	49.6	6.0	31.4	44.0	37.4	3.0	6.0	2.0	–	35.0	–	0.0
		< 3.5	74.3	7.5	8.2	–	15.7	10.8	8.3	5.0	–	–	3.6	56.6
		< 15	35.5	–	–	–	33.8	7.9	19.2	6.8	4.2	–	28.1	0.0
Leeds, UK	Clarke et al. (1984)	< 2.5	22.2	–	–	–	50.0	6.6	26.1	9.9	1.8	–	5.6	0.0
		2.5–15	13.3	–	–	–	13.3	5.8	7.4	2.5	8.2	–	62.8	0.0
Birmingham, UK	Harrison et al. (1997a)	< 10	25.7	18.0	20.0	–	38.0	6.0	17.0	6.0	2.0	–	–	31.0
Brisbane, Australia	Chan et al. (1997)	< 10	18.9	10.0	–	21.0	–	–	3.0	6.0	18.0	22.0	–	20.0
		< 2.5	7.3	19.3	–	27.0	–	2.6	5.0	10.0	9.7	6.1	–	20.3
Sapporo, Japan <sup>b</sup>	Kaneyasu et al. (1995)	2.5–10	10.4	2.8	–	13.0	–	4.3	1.4	2.7	22.0	29.0	–	24.7
		< 10	24.8	13.9	14.2	–	28.1	4.2	16.4	2.9	2.2	–	9.7	36.5
Lahore, Pakistan <sup>b</sup>	Smith et al. (1996)	TSP	607	2.9	13.1	–	16.0	2.1	3.0	1.2	–	–	16.4	61.3
Hong Kong <sup>b</sup>	Qin et al. (1997)	RSP	66.2	–	–	–	57.1	2.8	14.4	3.3	2.3	–	6.1	14.0
Antwerp, Belgium	Van Borm et al. (1989)	0.2–15	18.1	–	–	–	21.3 <sup>b</sup>	–	18.9	–	3.2	–	30.0	26.6

<sup>a</sup>Note. (1) TC = EC + OC; '–' means not measured.

<sup>b</sup>Indicates reconstructed.

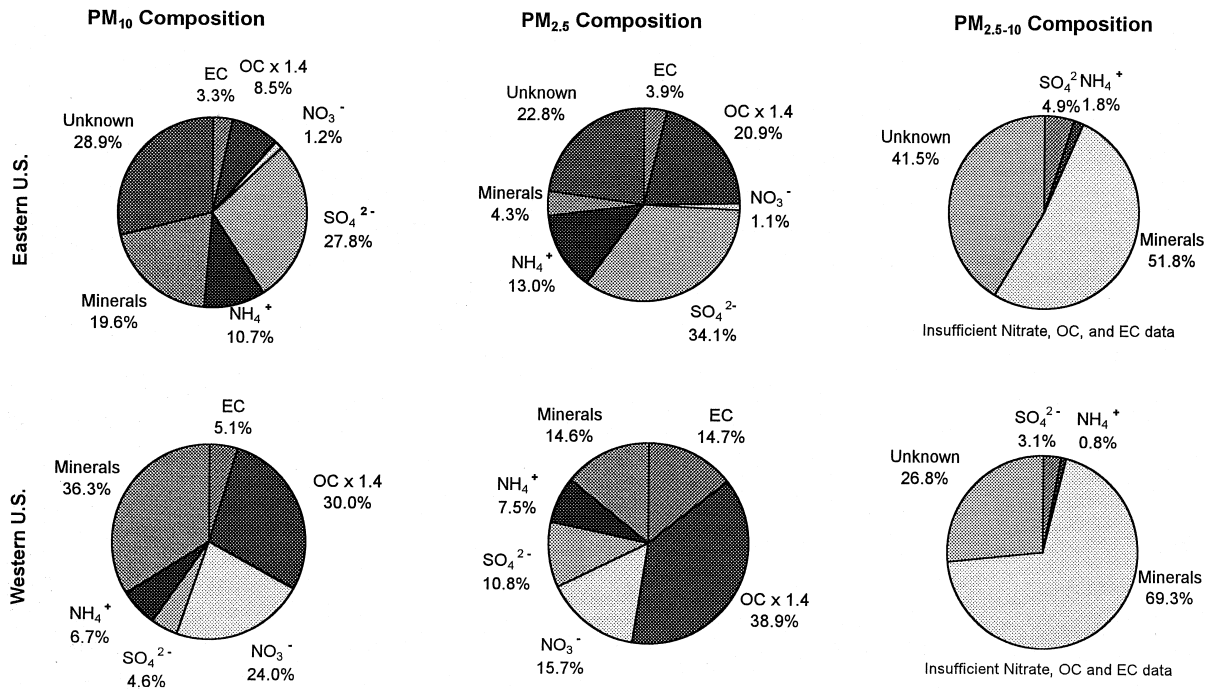


Fig. 1. Comparison of typical major component composition of airborne particulate matter from the eastern and western USA (USEPA, 1996).

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<sub>10</sub>).

#### 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 bio-availability 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

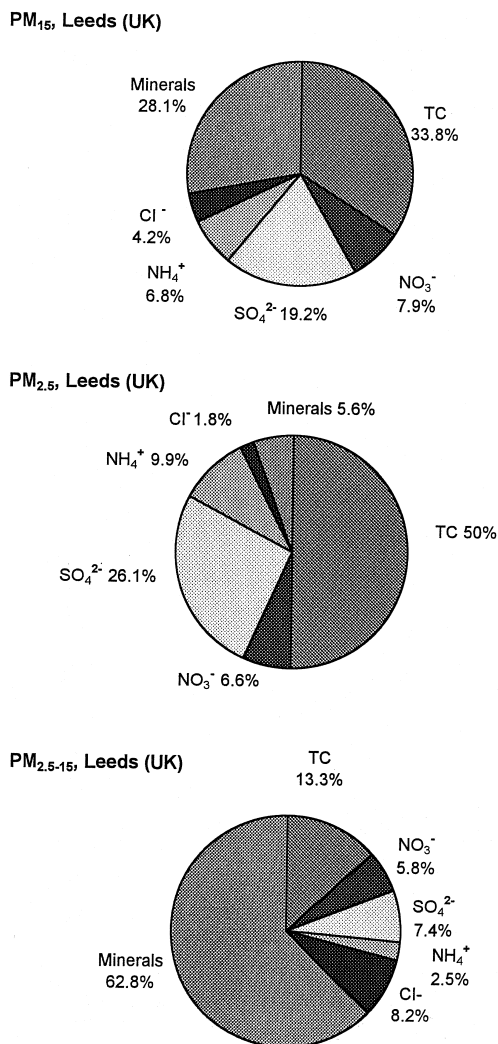


Fig. 2. Composition of airborne particulate matter sampled in Leeds, UK, 1982 (Clarke et al., 1984).

to see considerable differences between exposure-response functions for PM<sub>10</sub> 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



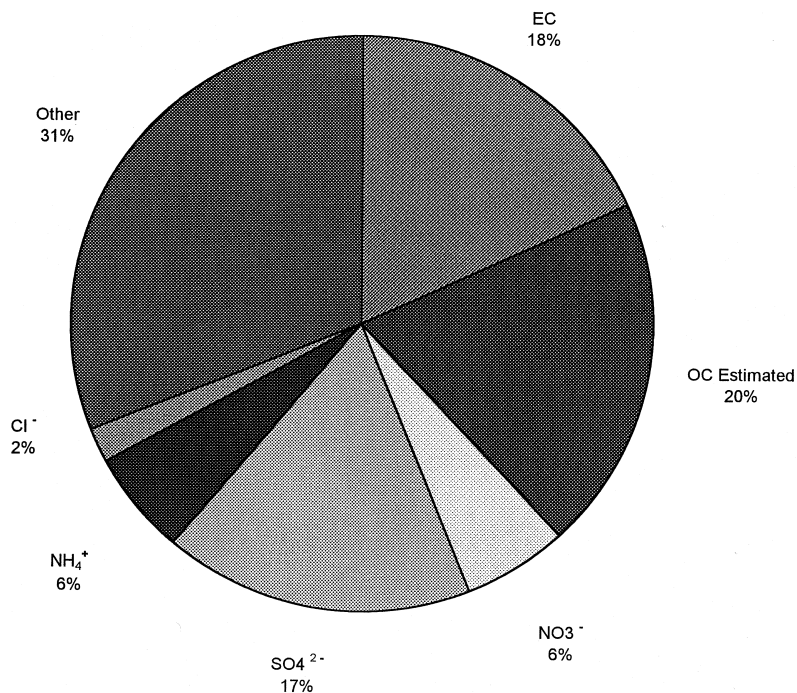


Fig. 3. Major component composition of PM<sub>10</sub> sampled in Birmingham, UK, 1995 (Harrison et al., 1997a).

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<sub>10</sub>, PM<sub>2.5</sub> and sulfate in each or the six cities, finding a stronger association for PM<sub>2.5</sub> than for sulfate, and it appears that as it is a major component of PM<sub>2.5</sub>, 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<sub>10</sub> to comprise sulfate-related fine particles, whereas in Rubidoux, California, sulfate comprised only 6.2% of PM<sub>10</sub> (Chow et al., 1992). Whilst, if sulfate represents a relatively constant proportion of PM<sub>10</sub>, it might

act as a surrogate in a time series study, if its relative abundance varies between locations then differences in the PM<sub>10</sub>-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<sub>2.5</sub> and mortality in six cities based on time series studies and shown little, if any, relationship with coarse particles in the 2.5–10- $\mu$ m 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)<sup>a</sup>

Species	Boston			Phoenix			Los Angeles		
	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.5 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.5 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.5 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )
Na	–	–	–	–	–	–	518	466	52
K	629	98	533	880	207	669	460	217	243
Ca	1139	70	1069	2100	170	1929	1190	335	854
Mg	–	–	–	–	–	–	287	75	212
Sc	–	–	–	–	–	–	–	–	–
Be	–	–	–	–	–	–	–	–	–
Cd	–	–	–	–	< 18	< 16	–	–	–
Sb	–	–	–	–	< 33	< 30	–	–	–
Al	3458	–	3458	2670	130	2539	847	250	597
Ti	154	–	154	140	< 30	121	165	60	106
V	28	20	8	–	< 16	< 14	9	7	3
Cr	8	4	4	10	3	8	42	25	17
Mn	30	1	29	50	23	32	63	43	21
Fe	1733	121	1612	1470	216	1259	2192	557	1635
Ni	34	12	22	10	3	3	5	7	–
Cu	58	35	23	40	15	21	178	273	–
Zn	100	46	54	90	56	34	293	298	–
As	3	2	1	–	< 20	< 2	19	15	4
Se	1	1	–	–	< 2	< 2	10	11	–
Sr	–	–	–	14	–	14	24	28	–
Pb	462	285	177	60	39	22	251	185	66
Si	6904	144	6760	7440	430	7013	2162	520	1642
Ba	–	–	–	10	< 106	< 77	127	43	84
Hg	–	–	–	–	–	–	–	–	–
Rb	–	–	–	–	< 2.5	3	–	–	–
Zr	–	–	–	–	–	–	–	–	–
Pd	–	–	–	–	–	–	–	–	–
Ag	–	–	–	–	–	–	–	–	–
In	–	–	–	–	–	–	–	–	–
Sn	–	–	–	–	< 28	< 26	–	–	–
La	–	–	–	–	–	–	–	–	–
Total mass	140 400	34 800	105 600	62 450	29 370	33 090	67 400	41 100	26 300

Table 2 (Continued)

Species	Chicago			Houston			St. Louis		
	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.5 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.5 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.5 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )
Na	22	22	< 17	< 1490	< 380	< 740	–	–	–
K	161	61	101	289	119	170	653	261	392
Ca	761	45	716	2935	155	2780	2949	132	2817
Mg	118	12	106	–	–	–	–	–	–
Sc	–	–	–	–	–	–	–	–	–
Be	–	–	–	–	–	–	–	–	–
Cd	< 41	< 29	< 12	< 12	< 3	< 6	5	4	1
Sb	< 59	< 42	< 17	6	6	< 9	7	6	1
Al	269	46	223	1216	123	1093	1412	203	1209
Ti	19	< 29	19	36	< 14	36	587	112	475
V	< 13	< 9	< 4	< 45	< 8	< 30	6	2	4
Cr	< 7.3	< 5	< 2.4	7	< 5	7	15	6	9
Mn	13	5	8	35	14	21	71	36	35
Fe	432	89	344	766	162	604	1493	275	1218
Ni	< 1.8	< 1	< 0.7	8	4	4	9	4	5
Cu	17	11	6	46	28	18	43	29	14
Zn	90	52	38	142	84	58	175	101	74
As	< 4.3	< 3	< 1.3	< 15	< 5	< 6	3	2	1
Se	< 1.7	< 1	< 0.6	< 3	< 2	–	5	4	1
Sr	–	1	–	–	< 2	< 8	9	2	7
Pb	32	27	5	589	465	124	877	688	189
Si	831	74	739	3200	210	2990	4928	458	4470
Ba	< 130	< 91	38	139	48	91	54	20	34
Hg	–	–	–	–	–	–	–	–	–
Rb	–	–	–	< 6	< 2	< 3	2	0	2
Zr	–	–	–	–	–	–	–	–	–
Pd	–	–	–	–	–	–	–	–	–
Ag	–	–	–	–	–	–	–	–	–
In	–	–	–	–	–	–	–	–	–
Sn	< 70	< 49	< 21	–	< 5	< 9	10	9	1
La	–	–	–	–	–	–	–	–	–
Total mass	28 540	13 570	14 970	63 400	38 600	24 800	62 000	34 000	28 000

<sup>a</sup>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  $\mu\text{m}$ ) in  $\text{PM}_{10}$ , ranging from approximately 20% in the winter to 50% in the summer months (Harrison et al., 1997a). Looking at data from across the USA,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  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  $\text{PM}_{2.5}$  are far more likely to be transferable than those based on  $\text{PM}_{10}$ , especially in

Table 3

Comparison of average urban concentrations for trace metals at different locations in Europe, Asia and USA<sup>a</sup>

Species	Birmingham UK <sup>1</sup>			Coimbra <sup>2</sup>			Lahore <sup>3</sup> TSP ( $\text{ng m}^{-3}$ )	Wageningen <sup>4</sup> Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )
	Fine < 2.1 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 2.1 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 0.95 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Coarse 0.95 – 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )		
Na	348	698	1050	360	1130	1490	2740	200.5
K	127	71.5	199	320	190	510	3300	367
Ca	40	168	208	520	1240	1760	4060	–
Mg	–	–	–	30	100	130	490	–
Sc	4.6	8.1	12.7	–	–	–	–	–
Be	–	–	–	0.2	0.1	0.3	9.2	–
Cd	–	–	–	1.5	0.2	1.8	43.4	–
Sb	–	–	–	0.4	0.5	0.9	–	–
Al	–	–	–	840	500	1340	37400	–
Ti	4.7	11.9	16.6	–	–	–	–	–
V	5.0	2.4	7.4	12.1	3.9	15.9	127	9.5
Cr	6.4	6.2	12.6	19.9	5.0	24.9	113	–
Mn	9.9	6.4	16.3	13.5	8.7	22.2	350	13
Fe	114.	187.	301.	190.	340	530	9930	425.5
Ni	2.9	1.9	4.8	4.9	1.2	6.1	79.7	–
Cu	30.2	8.5	38.7	22.4	17.8	40.2	420	22
Zn	297	55.6	353.	50.	20.	70.	27700	148
As	4.2	1.5	5.7	1.9	0.5	2.4	29.4	–
Se	2	1.1	3.1	0.6	0.2	0.8	–	–
Sr	–	–	–	–	–	–	–	–
Pb	73.9	17.1	91	250	60	310	3920	–
Si	–	–	–	–	–	–	–	649.5
Ba	–	–	–	–	–	–	–	–
Hg	–	–	–	–	–	–	–	–
Rb	–	–	–	–	–	–	–	–
Zr	–	–	–	–	–	–	–	–
Pd	–	–	–	–	–	–	–	–
Ag	–	–	–	–	–	–	–	–
In	–	–	–	–	–	–	–	–
Sn	–	–	–	–	–	–	–	–
La	–	–	–	–	–	–	–	–
Total mass	–	–	47000	29600	22500	52100	607000	35700

Table 3 (Continued)

Species	Arnhem <sup>5</sup>		Anaheim <sup>6</sup>		Azusa <sup>7</sup>		Edison <sup>8</sup>	
	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Total < 10 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )	Fine < 2.5 $\mu\text{m}$ ( $\text{ng m}^{-3}$ )
Na	327.	59	1659.3	231.8	1541.8	193.4	–	–
K	268.5	88	278.7	92.9	617.9	111.3	1378	1186
Ca	–	–	491	8.4	1304.7	150.4	1204	1043
Mg	–	–	348.8	36	604.5	55.4	–	–
Sc	–	–	–	–	–	–	–	–
Be	–	–	–	–	–	–	–	–
Cd	–	–	–	–	–	–	3	4
Sb	–	–	–	–	–	–	9	6
Al	–	–	701.2	35.1	2270.5	187.4	2684	1824
Ti	–	–	59.9	3.6	251	29.9	173	151
V	5.5	3.5	5.1	5.6	7.5	5.7	3	3
Cr	–	–	19.6	18.5	19.6	18	1	0
Mn	24.5	13	23.6	12.2	79.2	15.7	36	33
Fe	1168.5	241	598.9	29.6	1840.9	281.9	2140	1953
Ni	–	–	4.7	4.5	4.6	4.5	4	3
Cu	140	13.5	10.3	39.6	13.6	13.4	11	10
Zn	185	38	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	1139.5	147	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 Street and background sites in Wageningen (1/94) and Arnhem (10–11/94), Netherlands; 6 and 7 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.

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 4  
Particle count and mass measurements made in Birmingham, UK, 1995 (Harrison et al., 1999)<sup>a</sup>

Site <sup>b</sup>	Central Birmingham	Ward End	Hodge Hill
Mean particle count (1000 s particles cm <sup>-3</sup> )	36.6	28.6	96
Mean PM <sub>10</sub> (μg m <sup>-3</sup> )	23.6	23.5	PM <sub>10</sub> : 20.0 PM <sub>2.5</sub> : 13.0
PM/particle count (slope from regression line, ×10 <sup>-15</sup> g particle <sup>-1</sup> ) hourly values	0.4	0.38–0.46	PM <sub>10</sub> : 0.08 PM <sub>2.5</sub> : 0.07
PM/particle count (slope from regression line, ×10 <sup>15</sup> g particle <sup>-1</sup> ) daily values	0.35	0.3–0.37	PM <sub>10</sub> : 0.1 PM <sub>2.5</sub> : 0.08
Reciprocal of slope (×10 <sup>9</sup> particles μg <sup>-1</sup> ) hourly values	2.5	2.2–2.6	PM <sub>10</sub> : 12.5 PM <sub>2.5</sub> : 14.3
Reciprocal of slope (×10 <sup>9</sup> particles μg <sup>-1</sup> ) daily values	2.9	2.7–3.3	PM <sub>10</sub> : 10.0 PM <sub>2.5</sub> : 12.5

<sup>a</sup>Note. Data are aggregates of more than one sampling period at each site.

<sup>b</sup>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<sub>10</sub> 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<sub>10</sub> 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<sub>10</sub> 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<sub>2.5</sub>/PM<sub>10</sub> 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

Location	Nature of site	Sampling period	Instrument	Particle count and mass	Reference
Birmingham Centre, UK	Urban centre	13/9/94 – 23/10/94	TSI, 3025 CNC & TEOM	Mean particle count: $3.7 \times 10^4 \text{ cm}^{-3}$ Mean $\text{PM}_{10}$ : $23.6 \mu\text{g m}^{-3}$	Harrison et al. (1999)
Birmingham east, UK	Urban background	9–11/1995	TSI, 3022 CNC & TEOM	Mean particle count: $2.9 \times 10^4 \text{ cm}^{-3}$ Mean $\text{PM}_{10}$ : $23.5 \mu\text{g m}^{-3}$	Harrison et al. (1999)
Birmingham, Hodge Hill, UK	Urban background	–	CNC & TEOM	Mean particle count: $9.6 \times 10^4 \text{ cm}^{-3}$ Mean $\text{PM}_{10}$ : $20.0 \mu\text{g m}^{-3}$ Mean $\text{PM}_{2.5}$ : $13.0 \mu\text{g m}^{-3}$	Harrison et al. (1999)
Birmingham UK	Roadside	22/11/96 1–2/12/97	TSI, 3071 SMPS/CPC 3022	Mean particle count: $1.6\text{--}1.9 \times 10^5 \text{ cm}^{-3}$ <sup>a</sup> Mean $\text{PM}_{10}$ : $40.6 \mu\text{g m}^{-3}$	Shi et al. (1999)
Pasadena CA, USA	Urban	1–2/1996	TSI, 3071 DMA/CNC 3760 & MOUDI, 100	Mean particle count: $1.3 \times 10^4 \text{ cm}^{-3} \pm 8.9 \times 10^3$ $\text{PM}_{1.8}$ : $14.02\text{--}25.52 \mu\text{g m}^{-3}$	Hughes et al. (1998)
Erfurt City Germany	Urban	10/91–5/92	DEMA & OPC	Mean particle count: $1.8 \times 10^4 \text{ cm}^{-3}$ <sup>a</sup> Mean $\text{PM}_{2.5}$ : $73.8 \mu\text{g m}^{-3}$	Tuch et al. (1997)
Helsinki Finland	Urban centre and background	1/11/96– 1/5/97	TSI, 3010 & 3022 CPC; DMPS	Daily mean particle count: $2 \times 10^3\text{--}8 \times 10^4 \text{ cm}^{-3}$	Buzorius et al. (1999)
Brisbane Australia	Urban	–	SMPS	Particle count range: $5 \times 10^3\text{--}7 \times 10^4 \text{ cm}^{-3}$	Morawska et al., (1999)

<sup>a</sup> Derived from the particle volume data.

cle to  $PM_{10}$  relationships that any assessment will be experimentally difficult to conduct.

## References

- Adamson IYR, Prieditis H, Vincent R. Pulmonary toxicity of an atmospheric particulate sample is due to the soluble fraction. *Toxicol Appl Pharmacol* 1999;157:43–50.
- Amann CA, Siegl DC. Diesel particulates — what they are and why. *Aerosol Sci Technol* 1982;1:73–101.
- APEG. Source apportionment of airborne particulate matter in the United Kingdom. Airborne Particles Expert Group. Department of the Environment, Transport and the Regions. London, 1999.
- Bowman FM, Odum JR, Seinfeld JH, Pandis SN. Mathematical model for gas-particle partitioning of secondary organic aerosols. *Atmos Environ* 1997;31:3921–3931.
- Burton RM, Suh HH, Koutrakis P. Spatial variation in particulate concentrations within metropolitan Philadelphia. *Environ Sci Technol* 1996;30:400–407.
- Buzorius G, Hämeri K, Pekkanen J, Kulmala M. Spatial variation of aerosol number concentration in Helsinki City. *Atmos Environ* 1999;33:553–565.
- Chan YC, Simpson RW, McTainsh GH, 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.
- Chow JC, Watson JG, Lu Z et al. Descriptive analysis of  $PM_{2.5}$  and  $PM_{10}$  at regionally representative locations during SJVAQS/AUSPEX. *Atmos Environ* 1996;30:2079–2112.
- Chow JC, Watson JG, Fujita EM, Lu S, Lawson DR. Temporal and spatial variations of  $PM_{2.5}$  and  $PM_{10}$  aerosol in the southern California air quality study. *Atmos Environ* 1994;28:2016–2080.
- Chow JC, Liu CS, Cassmassi J, Watson JG, Lu Z, Pritchett LC. A neighborhood-scale study of  $PM_{10}$  source contributions in Rubidoux, California. *Atmos Environ* 1992;26A:693–706.
- Clarke AG, Willison MJ, Zeki EM. A comparison of urban and rural aerosol composition using dichotomous samplers. *Atmos Environ* 1984;18:1767–1775.
- Council of the European Communities, (1980). Council Directive of 15 July 1980 on Air Quality Limit Values for Sulphur Dioxide and Suspended Particulates. O.J., L229/30.
- Department of Health, 1995. Committee on the medical effects of air pollution. Non-biological particles and health. London: HMSO, 1995.
- Department of Health. Committee on the Medical Effects of Air Pollution. Quantification of the Effects of Air Pollution on Health in the United Kingdom. Stationery Office. London, 1998.
- Dockery DW, Pope CA, Xu X et al. An association between air pollution and mortality in six US cities. *N Engl J Med* 1993;329:1753–1759.
- Dockery DW, Pope CA. Acute respiratory effects of particulate air pollution. *Annu Rev Public Health* 1994;15:107–132.
- Donaldson K, MacNee W. The mechanism of lung injury caused by  $PM_{10}$ . Issues in Environmental Science and Technology, No. 10, Hester RE, Harrison RM, editors. Royal Society of Chemistry, 1998:21–32.
- Friedlander SK. Smoke dust and haze. New York: Wiley, 1977.
- Gilmour PS, Brown DM, Lindsay TG, Beswick PH, MacNee W, Donaldson K. Adverse health effects of  $PM_{10}$  particles: involvement of iron in generation of hydroxyl radical. *Occup Environ Med* 1996;53:817–822.
- Harrison RM, Allen AG. Measurements of atmospheric  $HNO_3$ , HCl and associated species on a small network in eastern England. *Atmos Environ* 1990;24A:369–376.
- 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.
- Harrison RM, Smith DJT, Pio CA, Castro LM. Comparative receptor modelling study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). *Atmos Environ* 1997b;31:3309–3321.
- Harrison RM, Jones M, Collins GC. Measurements of the physical properties of particles in the urban atmosphere. *Atmos Environ* 1999;33:309–321.
- Harrison RM, Jones M. The chemical composition of airborne particles in the UK atmosphere. *Sci Total Environ* 1995;168:195–214.
- Harrison RM, Kitto AMN. Estimation of the rate constant for the reaction of acid sulphate aerosol with  $NH_3$  gas from atmospheric measurements. *J Atmos Chem* 1992;15:133–143.
- Harrison RM, Msibi IM. Validation of techniques for fast response measurement of  $HNO_3$  and  $NH_3$  and determination of the  $[NH_3][HNO_3]$  concentration product. *Atmos Environ* 1994;28:247–255.
- Hughes LS, Cass GR, Gone J, Ames M, Olmez I. Physical and chemical characterization of atmospheric ultrafine particles in Los Angeles area. *Environ Sci Technol* 1998;32:1153–1161.
- Janssen NAH, Mansom KFMV, Jagt KVD, Harssema H, Hoek G. Mass concentration and elemental composition of airborne particulate matter at street and background locations. *Atmos Environ* 1997;31:1185–1193.
- Kaneyasu N, Ohta S, Murao N. Seasonal variation in the chemical composition of atmospheric aerosols and gaseous species in Sapporo, Japan. *Atmos Environ* 1995;29:1559–1568.
- Kao AS, Friedlander SK. Chemical signatures of the Los Angeles aerosol ( $dp < 3.5 \mu m$ ). *Aerosol Sci Technol* 1994;21:283–293.
- Kitto AMN, Harrison RM. Processes affecting concentrations of aerosol strong acidity at sites in eastern England. *Atmos Environ* 1992;26:2389–2399.
- Lippmann M. Background on health effects of acid aerosols. *Environ Health Perspect* 1989;79:3–6.
- Lippmann M. The 1997 US EPA standards for particulate matter and ozone, In Issues in Environmental Science and



- Technology, 10, Hester RE, Harrison RM, editors. Royal Society of Chemistry, 1998:75–99.
- Matthias-Maser S, Jaenicke R. Examination of atmospheric bioaerosol particles with radii  $> 0.2 \mu\text{m}$ . *J Aerosol Sci* 1994;25:1605–1613.
- Morawska L, Thomas S, Gilbert D, Greenaway C, Rijnders E. A study of the horizontal and vertical profile of submicrometer particles in relation to a busy road. *Atmos Environ* 1999;33:1261–1274.
- Oberdörster G, Gelein RM, Ferin J, Weiss B. Association of particulate air pollution and acute mortality: involvement of ultrafine particles? *Inhal Tox* 1995;7:111–124.
- Ostro BD. Associations between morbidity and alternative measures of particulate matter. *Risk Anal* 1990;10:421–427.
- Pope CA, Thunn MJ, Namboodiri MM et al. Particulate air pollution as a predictor of mortality in a prospective study of US adults. *Am J Respir Crit Care Med* 1995;151:669–674.
- Qin Y, Chan CK, Chan LY. Characteristics of chemical compositions of atmospheric aerosols in Hong Kong: spatial and seasonal distributions. *Sci Total Environ* 1997;206:25–37.
- QUARG. Urban Air Pollution in the United Kingdom. The First Report from the Quality of Urban Air Review Group. Department of the Environment. UK, 1993.
- QUARG. Airborne Particulate Matter in the United Kingdom. The Third Report from the Quality of Urban Air Review Group. Department of the Environment. UK, 1996.
- Schwartz J, Dockery DW, Neas LM. Is daily mortality associated specifically with fine particles? *Air Waste Manage Assoc* 1996;46:927–939.
- Seaton A, MacNee W, Donaldson K, Godden D. Particulate air pollution and acute health effects. *Lancet* 1995;345:176–178.
- Shi JP, Khan AA, Harrison RM. Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. *Sci Total Environ* 1999;235:51–64.
- Smith DJT. Source apportionment of atmospheric particles in the UK, Portugal and Pakistan. Ph.D. Thesis. University of Birmingham, 1995.
- Smith DJT, Harrison RM, Luhana L et al. Concentrations of particulate airborne polycyclic aromatic hydrocarbons and metals collected in Lahore, Pakistan. *Atmos Environ* 1996;30:4031–4040.
- 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.
- USEPA. Review of the Ambient Air Quality Standard for Particulate Matter: Policy Assessment of Scientific and Technical Information. OAQPS Staff Paper. EPA-452/R-96-013. Research Triangle Park. North Carolina, 1996.
- Van Borm WA, Adams FC, Maenhaut W. Characterisation of individual particles in the Antwerp aerosol. *Atmos Environ* 1989;23:1139–1151.
- Vasconcelos LAP, Macias ES, White WH. Aerosol composition as a function of haze and humidity levels in the southwestern US. *Atmos Environ*. 1994;28:3679–3691.
- WHO. Air Quality Guidelines for Europe. World Health Organisation European Office. Copenhagen, 1987.