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Measurement of number, mass and size distribution of particles in the atmosphere

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Typical size distributions for airborne particles are described and the significance of the ultrafine fraction highlighted. Size distributions may be expressed in terms of either mass (volume), surface area or number, and the interpretation of each is discussed together with appropriate measurement methods. The sources of ultrafine particles in the atmosphere include both primary emissions and secondary particles formed through homogeneous nucleation processes within the atmosphere. Examples of measurements of atmospheric ultrafine particles are given, highlighting situations with high concentrations of primary ultrafine particles and also situations where gas-to-particle conversion through homogeneous nucleation gives rise to bursts of new particle production. Finally, the relationship between particle mass and number within the atmosphere at a polluted site is examined.

Keywords: ultrafine particles; particle size distribution; particle nucleation processes; road-traffic emissions

1. Introduction

Atmospheric particulate matter is inherently more difficult to study than gas-phase components of the atmosphere. It is highly variable in size and in chemical composition, and, indeed, individual particles may have a very complex make-up (Harrison & van Grieken 1998). Simple spectroscopic techniques which can be applied to qualitative and quantitative analysis of gas-phase species in the atmosphere are not applicable in useful ways to the determination of aerosol composition. The subject therefore progressed rather slowly as a topic of research until it received three major stimuli in the 1980s. These were as follows.

(a) Recognition of the importance of airborne particles through both direct and indirect mechanisms as regulators of global climate (Horvath 1998). Direct mechanisms relate to the absorption and scattering of solar and terrestrial radiation, while the indirect mechanisms, which may ultimately prove more important, operate through the role of airborne particles as cloud condensation nuclei (Charlson *et al*. 1987).

(b) Discovery of the Antarctic ozone hole and a recognition that reactions on polar stratospheric cloud particles were key to the chemistry leading to dramatic ozone depletion.

Table 1. *Influence of particle size on particle number and surface area for a given particle mass*

particle diameter (μm)	relative number of particles	relative surface area
10	1	1
1	10^3	10^2
0.1	10^6	10^4
0.01	10^9	10^6

(c) The discovery that both acute and chronic exposure to airborne particles is associated statistically with a range of adverse health outcomes and a growing acceptance that these relationships are causal (COMEAP 1995).

In both the first and last of these areas, ultrafine particles are a source of especial interest. In the case of climate regulation, one of the key areas of interest is the atmosphere over the oceans, where cloud condensation nuclei develop from the growth of new initially ultrafine particles formed by gas-to-particle conversion processes (Charlson *et al*. 1987). In the area of human health, toxicological studies using rat models have shown that ultrafine particles are considerably more toxic per unit mass than coarser particles of the same material (Donaldson & MacNee 1998). Additionally, one of the hypotheses explains the unexpected link between particulate matter exposure and cardiovascular disease outcomes in terms of the capability of ultrafine particles to penetrate the pulmonary interstitium (Seaton *et al*. 1995).

This paper will set the background to many of the subsequent papers on research on airborne particulate matter by describing the origins and measurement methods for airborne particles, the interrelationship between methods and measurements, and by giving some examples of particle measurements illustrative of specific phenomena in the atmosphere.

2. Size distribution of particles in the atmosphere

There are three distinct modes into which airborne particles can typically be divided. These may be described as follows.

(a) *Transient nuclei mode.* These are particles typically less than *ca.* 100 nm in diameter, which are relatively newly formed, having arisen from the condensation of involatile materials to form new particles which subsequently grow by condensation processes. The formation can occur both in hot combustion gases and in metallurgical processes, involving, for example, the condensation of lead atoms from the vapour to form particles, or within the atmosphere itself from chemical reactions of gases to form involatile species which condense to form particles. In order for new particles to form through a process known as homogeneous nucleation, a very substantial supersaturation of vapour needs to occur. The only clearly recognized example of this process in the atmosphere is the oxidation of sulphur dioxide to sulphuric acid, which is able to undergo binary nucleation with water or ternary nucleation with water and ammonia (Korhonen *et al*. 1999). It is likely that most new particles formed in the atmosphere arise from this oxidation process, although subsequent particle growth

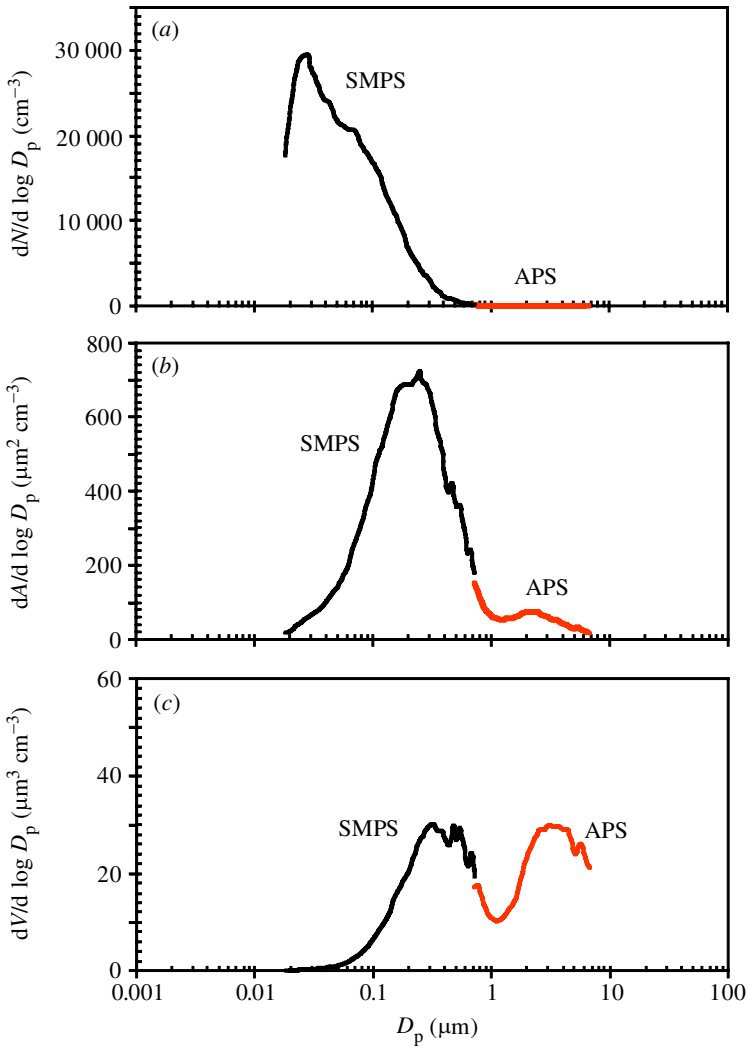

Figure 1. A measured particle size distribution from suburban Birmingham, weighted by (*a*) number, (*b*) surface area, and (*c*) volume.

may be enhanced through condensation of semi-volatile organic compounds (Marti *et al*. 1997). Newly formed nucleation mode particles are typically of the order of 1–2 nm in diameter, but rapid growth generally ensues. The mode in the number distribution of nucleation mode particles is typically *ca.* 20–30 nm in diameter.

(b) *Accumulation mode.* Particles in the transient nuclei mode can grow both by condensation of low volatility materials and through coagulation. In doing so they are likely eventually to enter the accumulation mode which describes particles between *ca.* 100 nm and 2 μm in diameter. Accumulation mode particles are subject to rather inefficient loss from the atmosphere by wet and dry deposition processes and, because of their low number concentration, are not subject to significant further growth

through coagulation. They have an atmospheric lifetime of several days and can therefore travel over very long distances within the atmosphere.

(c) *Coarse particle mode.* After a minimum in abundance at *ca.* 1–2 μm, there is a subsequent growth in particle abundance (in terms of mass but not number) for particles which extend in size up to *ca.* 100 μm, although above 10 μm diameter their atmospheric lifetime becomes rather short. These coarse mode particles are formed through mechanical attrition and disintegration processes such as the formation of sea spray from bubble bursting in the ocean and the wind-blown suspension of land surface dusts and soil. They therefore arise quite differently from transient nuclei and accumulation mode particles and can be quite distinct in their chemical composition (QUARG 1996).

The term *ultrafine particles* does not have a universally agreed definition but is widely accepted as describing particles of less than 100 nm in diameter. The further widely used term *nanoparticles* again has no universally agreed definition, but is widely used to describe particles of less than 50 nm in diameter.

Airborne particles are most frequently measured as either number-weighted or mass-weighted distributions. Because of the cube dependence of volume and, thus, mass on diameter, the two kinds of distribution look extremely different. Figure 1 illustrates this through plotting the number-weighted, surface-area-weighted and mass-weighted distributions of atmospheric particles measured in Birmingham, UK. Measurements were made using a scanning mobility particle sizer (SMPS) and aerodynamic particle sizer (APS) simultaneously to capture the smaller and larger ends of the particle size distribution, respectively. Reference to table 1 gives a clearer insight into the mathematics, whereby 10^9 particles of 10 nm diameter have the same mass as 1000 particles of 1 μm diameter or one particle of 10 μm diameter. Thus, the extremely numerous particles in the transient nuclei mode may represent only a very small proportion of total particle mass. Conversely, the very significant mass of particles in the coarse particle mode are very few in number. In simple terms it is likely that the bulk of the particle number is in the transient nuclei, the surface area is predominantly in the accumulation mode, and the volume, and hence mass, is divided between the accumulation mode and coarse particle mode. Ultrafine particles typically dominate the particle number count, make a significant contribution to surface area, but very little to mass, as shown in figure 1.

3. Sources of ultrafine particles

Particles in the atmosphere may be either

(a) primary, which refers to particles emitted directly from sources such as road traffic and industry; or

(b) secondary, which refers to particles formed within the atmosphere from gas-to-particle conversion processes.

Inventories of primary particle emissions are widely available and generally do a good job in describing the well-defined sources such as road-vehicle emissions, but there are very substantial uncertainties in their estimates of such sources as wind-blown dust and resuspension from road traffic. Many inventories do not include

such source categories. The majority of such inventories relate to emissions of PM_{10} or particles which pass a sampling inlet with a 50% exclusion efficiency at 10 μm. There is a national inventory of ultrafine particles for the UK which is shown in figure 2. Compared with the inventory for PM_{10}, the ultrafine particles emissions inventory gives far greater relative importance to emissions from road vehicles (60%) as opposed to the PM_{10} inventory (25%). Other combustion and metallurgical sources also contribute to ultrafine particle emissions to the atmosphere. In practice, ground-level concentrations of primary PM_{10} correlate very strongly with local road-traffic emissions, and this is likely to be the case especially for ultrafine particles. Indeed, observations of particle number counts, which reflect primarily the abundance of ultrafine particles, have shown that such particles provide an excellent tracer of road-vehicle traffic emissions (Harrison *et al.* 1999*a*).

Homogeneous nucleation to form new particles is especially favourable in environments with a low pre-existing particle surface area, which acts as a competitive site for condensation. Therefore, homogeneous nucleation is expected to be important primarily in remote areas, and, indeed, quite spectacular bursts have been reported in the coastal zone, although the precise mechanisms are not fully understood (Allen *et al.* 1999; O'Dowd *et al.* 1999). There are also a small number of convincing observations of homogeneous nucleation to form new particles in the urban atmosphere. Current nucleation theories are limited in their ability to predict such phenomena, although the recent development of a theory for ternary nucleation may offer added insight (Korhonen *et al.* 1999).

4. Measurement methods for particulate matter

A large variety of instruments is available, many of them through commercial suppliers, for the measurement and characterization of airborne particles. Within the scope of this article it would be possible to describe only a few of the most commonly used procedures. No endorsement of specific techniques or manufacturers is implied.

(*a*) *Particle number*

This is measured through use of condensation nucleus counters (CNCs), which have been available in manual form, such as the Nolan–Pollack counter, for many years, and more recently in the form of continuous devices. The continuous CNC instruments are typically based on drawing particles through a zone which is saturated with n-butanol vapour, which is subsequently cooled to cause condensation of the vapour on the particles (Stolzenburg & McMurry 1991). This causes the particles to grow to the order of 10 μm diameter, at which they are very effective light scatterers and they are monitored at low number density through counting the signals from particles as they pass through a light beam, or at higher number densities through a photometric mode which determines 90° scattered intensity of incident light. The lower size cut-off of such instruments is dependent on design and the degree of supersaturation achieved, but typically varies in commercial instruments from 3 nm in ultrafine particle counters to 10 or 20 nm in less-sophisticated devices. The upper size limit is determined by the aspiration efficiency of the inlet and is likely to be *ca.* 5 μm. One application of particle counters to the determination of newly formed particles is using two counters in tandem, one of which has a lower

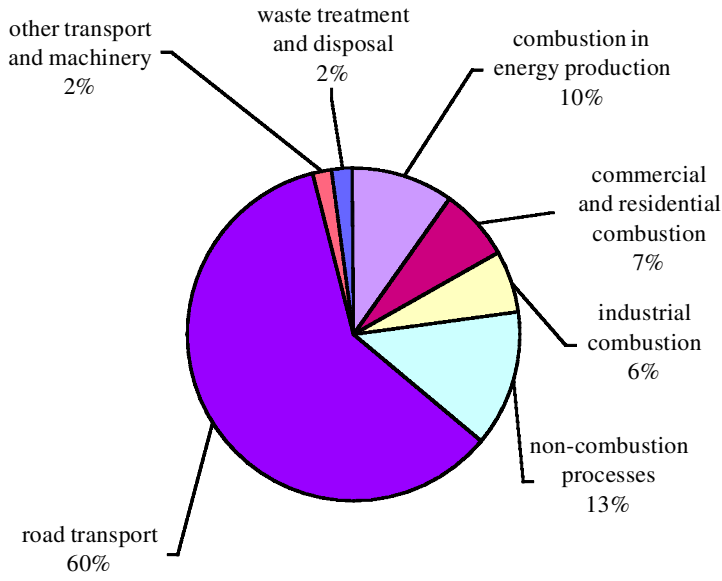

Figure 2. Pie chart illustrating the sources of $PM_{0.1}$ emissions in the UK in 1996 (APEG 1999).

cut-off (50% efficiency) of 3 nm, the other with a lower cut-off of 7 or 10 nm (Grenfell *et al.* 1999). The difference in particle number count corresponds to particles in the 3–7 nm diameter size range, which represent particles which have grown slightly from newly formed particles.

The condensation nucleus counter forms part of a device for measuring particle number size distributions. Such instruments typically use a combination of an electrostatic classifier and condensation nucleus counter. The function of the electrostatic classifier is to separate particles on the basis of their electrical mobility, which is a function of particle diameter. The electrostatic classifier, termed a differential mobility analyser, is 'tuned' through a combination of flows and voltage to transmit only one diameter of particles at a time (Hinds 1999). The number density in this size is measured subsequently with the condensation particle counter. By scanning the voltage in the electrostatic classifier, different particle sizes may be transmitted sequentially and a complete size distribution built up over a period of a few minutes. Such instruments are now being deployed within a small UK measurement network.

(*b*) *Particle mass*

Classically, particle mass has been determined by collecting airborne particles by filtration and weighing the filter before and after particle collection. In order to restrict the particles to a given size range, such as PM_{10}, $PM_{2.5}$ or $PM_{1.0}$, size-selective inlets are available which restrict the particles allowed access to the filter. Such samplers may be termed either high volume or low volume depending on the airflow rates. In UK networks, both PM_{10} and $PM_{2.5}$ are measured continuously using tapered element oscillating microbalance (TEOM) samplers. In these instruments, particles are collected on a small filter which is located on the tip of a tapered glass element which forms part of an oscillation microbalance. The oscillation frequency of the microbalance changes with the mass of particles collected on the filter. One facet

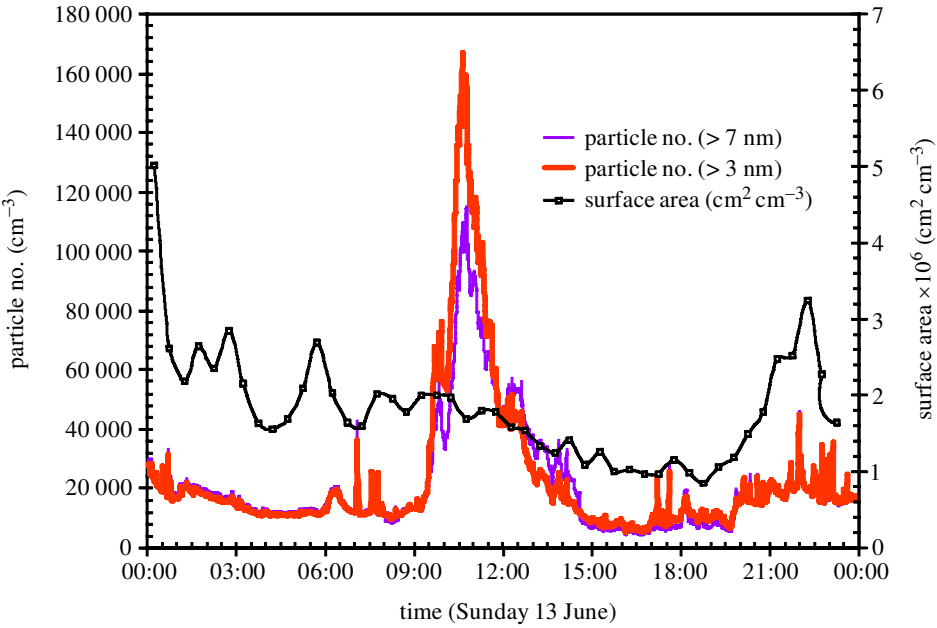

Figure 3. Particle number count, greater than 7 nm and greater than 3 nm, and surface area on 13 June 1999 in suburban Birmingham.

of these instruments is that the inlet airstream is typically heated to 50 °C, which leads to an almost complete loss of semi-volatile particles, which in some situations can represent a significant proportion of particle mass. In the UK atmosphere, TEOM instruments typically measure concentrations of PM_{10} some 20–30% lower than the more conventional so-called gravimetric samplers (APEG 1999).

To date, no such instrument has been designed specifically for the determination of ultrafine particle mass. Estimates of the mass of particles less than 100 nm in diameter can be made through collecting particle samples in a size-fractionated manner using cascade impactors, which depend upon the inertial properties of particles to separate them into different size bands. Plotting of the full size distribution and making a cut at 100 nm would allow an estimate of ultrafine particle mass, although this is rarely measured. Loss of semi-volatile materials can be a major problem in the lower pressure impactors typically used for separating ultrafine particles.

(*c*) *Surface area*

This is rarely measured directly, although a device called an epiphaniometer has been described, which determines the Fuchs surface area of particles (Gaggeler *et al*. 1989). It does so by attaching a gaseous radionuclide to the particle surface and counting collected radioactivity. The physics of radionuclide attachment is not a simple single function of surface area across the entire particle size range, and particles significantly greater in diameter than the mean free path of the gas molecules offer a significant diffusion resistance to radionuclide attachment. Surface areas may also be estimated indirectly from measurements of particle size distribution, provided the particle geometry is known or assumed.

5. Examples of measurements of atmospheric ultrafine particles

Four examples are given of measurements of particles in the ultrafine size range, illustrating a substantial range of environments.

(a) *Mace Head, Ireland*

Mace Head is on the west coast of Ireland and frequently experiences relatively clean marine airmasses. Observations over a period of years have shown massive bursts in new particle formation at Mace Head, which, from their nature and from measurements offshore, are known to occur within the coastal zone (Allen *et al*. 1999). Particle number densities can well exceed 10^5 cm^{-3}, which is immense in comparison with background concentrations of particles in marine air at Mace Head, typically of the order of 100–500 cm^{-3}. Not only do particle number concentrations go to very high levels, a large proportion of the particles are in the 3–7 nm diameter size range and are, therefore, reflective of very newly formed particles. The mechanism of particle formation at Mace Head is not fully understood, but an intriguing observation is that the particle bursts appear to occur only in daytime and predominantly at low tide (Allen *et al*. 1999). It therefore seems likely that some substance, probably organic in nature, released from marine macroalgae at low tide, plays a major role in particle formation and/or growth. Most probably the nucleation process involves sulphuric acid, probably in combination with water vapour and ammonia, but rapid particle growth depends on the availability of low-volatility organic matter, probably originating from atmospheric oxidation of highly reactive organic compounds released from the macroalgae in the coastal zone. Similar observations have been made at other coastal sites, but appear to depend on a rocky coastline suitable for macroalgal growth (Mihalopoulos *et al*. 1992).

(b) *Weybourne, north Norfolk*

Measurements in the summer of 1995 at the Weybourne site on the north Norfolk coast showed substantial bursts in particle number concentration which were not accompanied by an increase in surface area as measured by the epiphaniometer (Harrison *et al*. 2000). Closer examination of these data showed that, unlike Mace Head, there was no relationship to the tidal cycle. However, the nature of the coastlines is quite different, with no exposure of rocks and macroalgae at Weybourne at low tide. The largest bursts in new particle production occurred in polluted air travelling from the land towards the sea, and the onset of particle production corresponded to the increase in solar radiation capable of photolysing ozone to form excited state oxygen atoms, which in turn lead to the formation of hydroxyl radicals. These hydroxyl radicals are responsible for the oxidation of sulphur dioxide and also the rapid oxidation of many organic compounds, therefore leading to the production both of sulphuric acid vapour, capable of nucleation, and of oxidized organic compounds, which can contribute to particle growth.

(c) *Suburban Birmingham*

Measurements with tandem particle counters and of size distributions using a scanning mobility particle counter, shown in figures 3 and 4, respectively, have shown

clear evidence on a small number of occasions of new particle production within the suburban atmosphere of Birmingham. Thus, it is seen in figure 3 that between 09:30 and 12:00, there is a substantial burst in particle number concentration containing an appreciable proportion of particles in the 3–7 nm diameter range. The plot of size distribution versus time in figure 4 clearly shows that at around 10:15 the peak in the number distribution comes within range of the scanning mobility particle sizer at *ca.* 10 nm and steadily grows over a period of 2 h to *ca.* 27 nm. Such nucleation and growth processes are currently the subject of intensive research activity.

(*d*) *Twin site measurements in London*

Measurements of PM_{10}, $PM_{2.5}$, traffic-related gases, particle number and size distribution are made on a continuous basis at two nearby sites in central London. London Marylebone Road is a site located adjacent to one of the busiest roads in central London, carrying *ca.* 70 000 vehicles per day. About 2 km distant, the site of London Bloomsbury is a central urban background site, where the monitoring station is located within the centre of an urban square. Data are archived on an hourly basis and differences calculated between the two sites, which are taken to be representative of the roadside increment due to traffic at the Marylebone Road location (APEG 1999). The data show a much elevated particle number concentration and a moderately elevated mass concentration at the Marylebone Road site, with the traffic increment in the particle size distribution having a mode in the number-weighted distribution at *ca.* 20 nm diameter, well below that recorded using conventional dilution tunnel methods in many of the studies of engine exhaust, which we have shown to give an unreliable estimate of size distribution (Shi & Harrison 1999). Particle number counts show substantial variations with time of day, reflective of road-traffic activity and prevailing meteorological conditions, as exemplified by figure 5, which shows a large morning rush-hour peak from 06:00 to 10:00.

6. Relationship of particle mass and number within the atmosphere

As noted above, particle number concentrations are dominated by particles in the transient nuclei mode, whereas the volume and, hence, mass lies predominantly in the accumulation and coarse particle ranges. There is therefore no necessity that the number and mass concentrations should be especially well correlated. If it were the case that the effects of particles on human health were driven by the ultrafine fraction, then it might be surprising if epidemiological studies using PM_{10} mass as the metric of particle concentration were to show a correlation with adverse health outcomes.

In practice, because fine particles (less than 2.5 μm) tend to form a relatively constant proportion of PM_{10} mass, and because the majority of such particulate matter arises from secondary sources and a small number of primary combustion-related sources, particle number and mass tend to be broadly correlated within the atmosphere. Thus, for example, at the London Marylebone Road site, particle number concentration and mass are quite strongly correlated in the road-traffic increment ($r = 0.72$), and in a study at a background site in central Birmingham a quite strong correlation between PM_{10} mass and number count ($r = 0.66$) was also observed (Harrison *et al.* 1999*b*). Such correlations are likely to be sufficiently strong as to

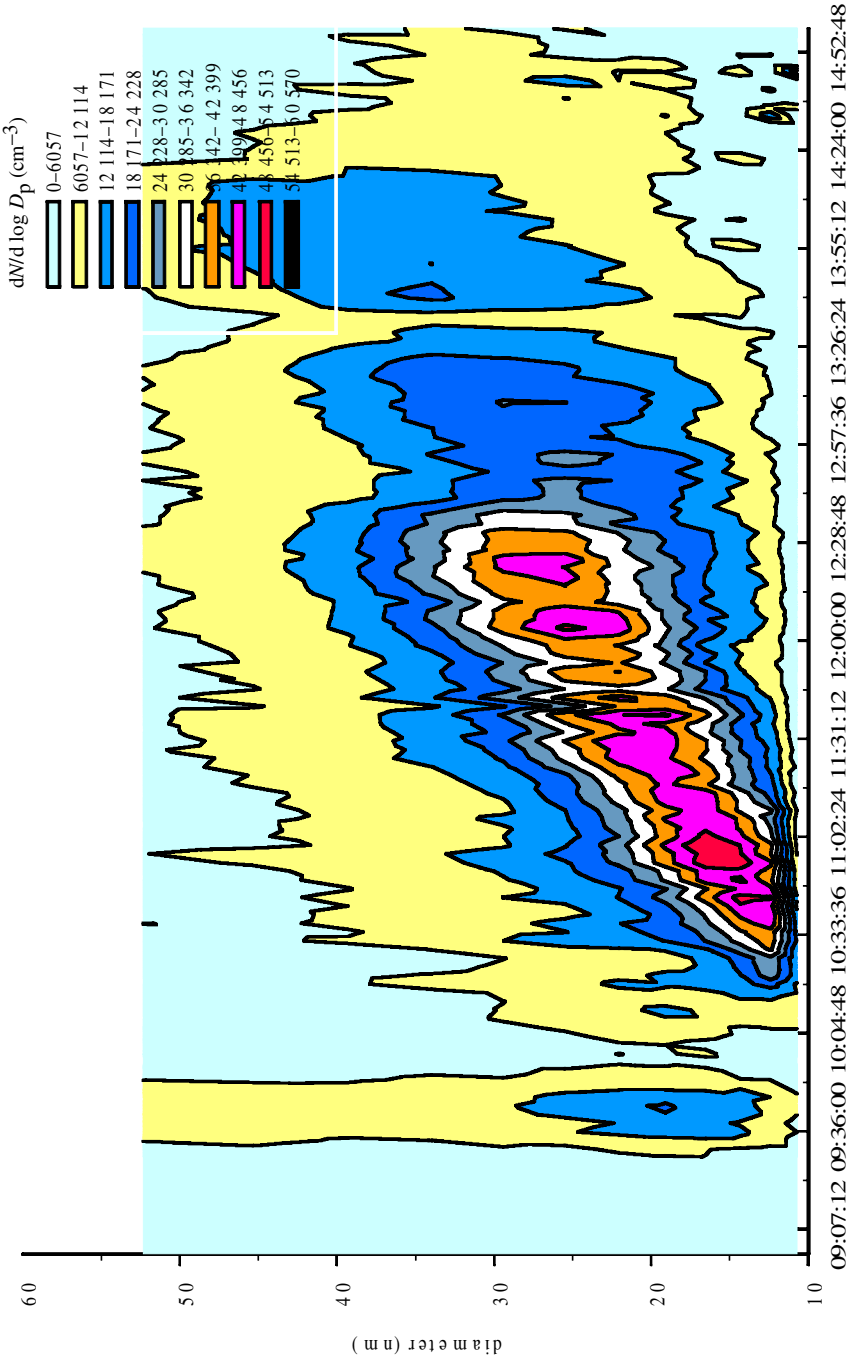

Figure 4. The evolution of the particle size distribution during a nucleation event on 13 June 1999 (see figure 3).

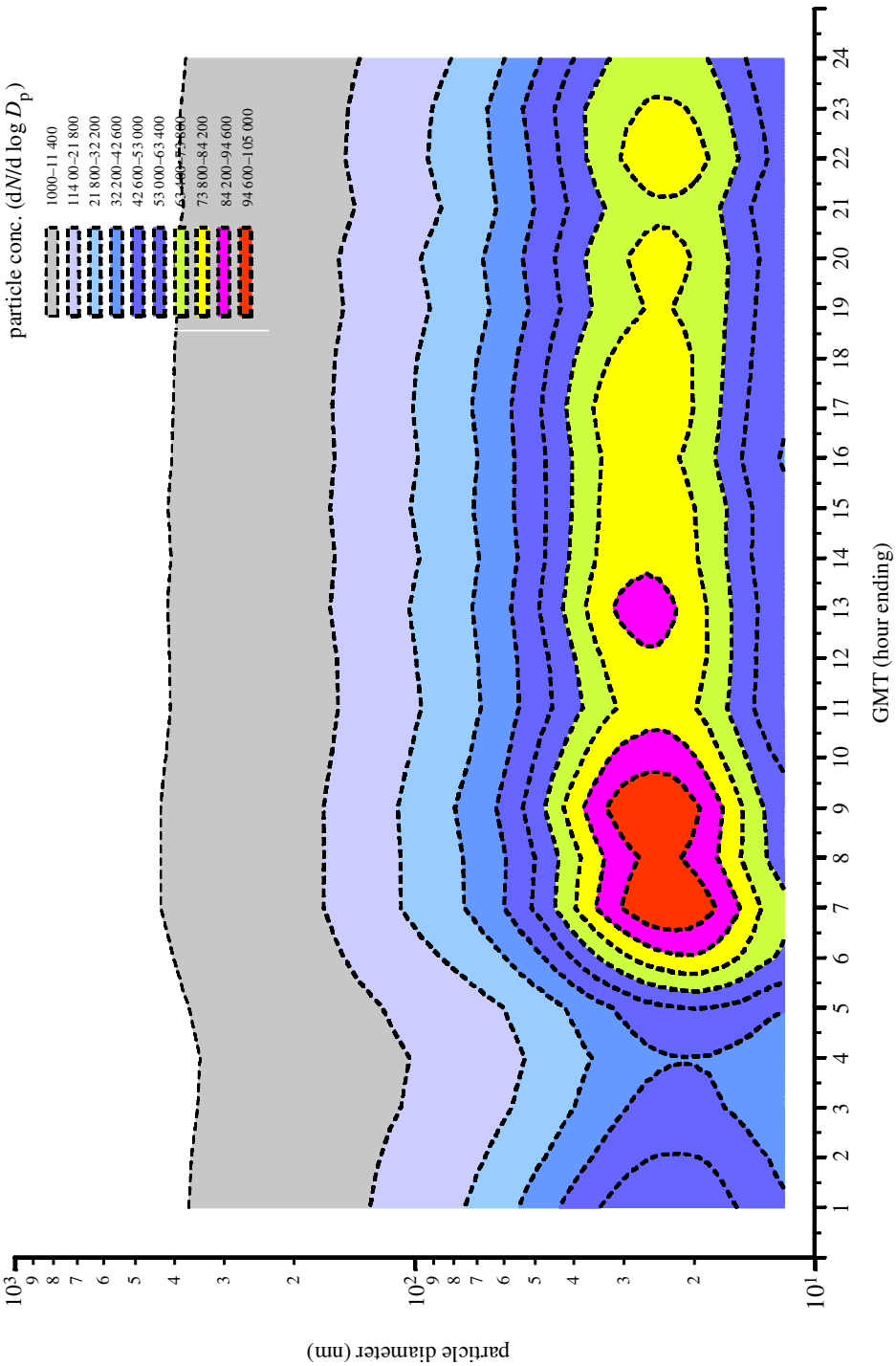

Figure 5. Average diurnal plot of particle size distributions for April and May 1998 at London, Marylebone Road.

obscure any ability to clearly differentiate through epidemiological studies between PM_{10} mass and particle number as the causal agent in driving adverse health outcomes, at least in the UK urban areas within which our measurements have been taken.

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Discussion

M. S. Bingley (*Cobham, UK*). Catalytic convertors take 10 min to warm up and start working. During this period, exhaust gas emissions will be rich ($\lambda < 1.0$). Will this add ultrafine particles to the atmosphere of urban areas during this period?

R. M. Harrison. The operation of a petrol engine under fuel-rich conditions with a cold catalytic convertor is likely to lead to enhanced production of ultrafine particles, although I am not aware of any research into this issue. It should be borne in mind, however, that under ever-tightening emissions-control legislation, catalytic convertors are being designed to higher standards, such that they become effective far more rapidly than in the past.

M. Wallis (*FoE Cymru, Cardiff, UK*). In the $PM_{0.1}$ inventory that you presented, the UK's industrial fraction of 10% surely has lower importance at street level. Particle lifetime and transport are relevant for estimating human exposure, so should we rate industrial sources as significant?

R. M. Harrison. The industrial contribution to $PM_{0.1}$ emissions in the UK is greater than 10%. Industrial combustion and industrial processes together account for 19% of the inventory total, and a proportion of the 3% from waste treatment and disposal and 10% from combustion in energy production and transformation are also attributable to industry. Monitoring of the atmosphere clearly shows an elevation of ultrafine particle concentrations within plumes from higher temperature sources and I have no doubt that industrial sources are significant in many locations.

Unknown speaker. There appear to be anomalies in the PM_{10} data presented in the report by APEG (1999). In northeast Derbyshire in January 1997, figures approached 58 $\mu g\ m^{-3}$, which were found again in independent monitoring by another government quango in 1998. Yet, in the balance of 1997, figures went as low as zero to end up with an annual average of 26 $\mu g\ m^{-3}$, which just happens to be the figure presented to the EC for the UK. I have printouts of minus readings all over the UK, which appear as serious as a colleague's discovery of a $-17\ \mu g\ m^{-3}$ council monitor reading near a cement works when Environment Agency independent findings of 240 $\mu g\ m^{-3}$ had been published months earlier. Can you comment on the need for rigorous calibration of monitors and accuracy of computer analysis and modelling?

R. M. Harrison. It is not possible to comment on the specific 'anomalies' raised in the question without sight of the datasets being cited. Data in the APEG (1999) report were from reputable organizations and I have no reason to doubt their quality.

Clearly, there is a need for rigorous calibration procedures and an awareness that instrumental analysers working on different principles measure different properties of the particles and, therefore, may give different measurements of 'mass'. The ultimate calibration of a truly gravimetric instrument can, however, be obtained through laboratory weighing of collected involatile particles. Numerical models are only as accurate as the input data and their physical descriptions and parametrizations of environmental dispersion processes. They are not able to give wholly accurate predictions, but nonetheless can be extremely useful in providing a guide to ground-level concentrations.

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