High Temporal Resolution Measurements of Roadside Particle Size Distributions and Their Implications for Exposure

A S Tomlin, D T Young, J J N Lingard and E L Agius

Energy and Resources Research Institute, University of Leeds, Leeds, LS2 9JT, UK

A.S.Tomlin@leeds.ac.uk

Abstract High time resolution, size segregated studies of ultrafine particle number concentrations (PNC) were performed at two UK roadside locations using a DMS500 particle spectrometer including sampling with and without a thermodenuder. Intercomparisons between the DMS500, an SMPS and a CPC, indicate that the SMPS can underestimate PNC due to the transient nature of excursions in concentrations and the longer scan time of the instrument. Short duration transient periods of high number concentrations made considerable contributions to hourly average PNC. The transient nature of changes in PNC potentially affects the type of exposure experienced in the roadside environment, as well as indoor outdoor exchange. The transient shifts were dominated by Aitken mode particles during high traffic periods, with the Aitken mode comprised of internally mixed particles with a low volatility core (thought to be primarily soot) and a surface of condensed and absorbed material. Transient periods of high nucleation mode PNC were also found, but were relatively more important during night-time and afternoon periods, due to secondary formation processes and lower concentrations of pre-existing particles. The thermodenuder studies indicated the presence of highly volatile liquid droplets in the nucleation mode which were lost on heating. Transient events and complexities in particle mixing state within the ultrafine fraction, coupled with discrepancies between instruments, make the potential adoption of a total number based air quality standard more complicated than first appears. Nucleation mode particle numbers are highly dependent on atmospheric and traffic conditions as well as pre-existing particle surface area and may be toxicologically less significant if they are predominantly liquid droplets. Aitken mode particles have been shown in previous studies to have higher toxicological significance due to their chemical composition. Their hourly average PNC correlated well with PM$_{2.5}$ and estimated PM$_{1}$ with lower significance of equivalent correlation of nucleation mode particles.

1. Introduction

Air quality standards for particulate matter in the UK are currently based on 24 hour and annual means for PM$_{10}$ concentrations, where PM$_{10}$ represents the mass of particles that can pass through a size selective inlet with a collection efficiency of 50% for particles of aerodynamic diameter 10µm. In order to comply with standards, control efforts are therefore aimed at reducing the mass of particles below 10µm, and current European engine emission standards are PM$_{10}$ based. A number of studies have shown that PM$_{10}$ within UK urban areas can be dominated by the coarser fraction, and have indicated a lack of correlation between the numbers of ultrafines (Uf) and PM$_{10}$, particularly at background sites. Whilst Uf ≤ 100 nm in diameter (Dp) only contribute 1 to 20 % of the particle mass,
they can represent >90% of the total PNC in a diesel exhaust [1] or at an urban roadside [2]. It follows that achieving the current standards will not necessarily lead to a reduction in the numbers of Uf particles, although this would depend on the sources of the emissions under control. Since engine emissions are dominated by smaller particles, control technologies aimed at reducing overall mass would have a positive impact reducing parts of the Uf fraction. On the other hand, some studies indicate that as particle mass concentrations in ambient air decrease, increased levels of particle numbers are detected [3]. Proposals for a PM$_{2.5}$ based standard are under discussion and would also help to focus controls to the finer fractions. However, toxicological studies have suggested that high numbers of Uf particles in the atmosphere can contribute to inflammatory responses and this raises the question as to whether mass based standards are the optimal way to reduce the impact of particulate pollution on health [4]. The possible additional use of a number concentration based standard for emissions has been outlined in proposals for Euro VI legislation for light duty vehicles (EC regulation No 715/2007).

There are a growing number of studies which aim to compare the use of different measures of particle concentration in terms of their association with end health effects such as daily mortality, hospital admissions [5], cardiorespiratory symptoms [6], stroke mortality [7] and asthma medication use [8]. Many studies suggest stronger associations of fine particles (PM$_{2.5}$) with effects such as hospital admission by age [5], respiratory symptoms [6,9] and peak expiratory flow, than coarse particles [9], with particular emphasis on fine sulphate particles in [9]. There are conflicting results on the influence of ultrafines with some studies showing weaker associations of ultrafines than fines with certain health outcomes [6,10] and others showing comparable effects [7]. The chemical complexity and daily, seasonal and spatial variability in the composition within the particle size distribution is a possible reason for the lack of consensus between different studies. Perhaps one area of concern is the presence of semi-volatile material within ambient particles which may not be well understood from a toxicological point of view, and in addition can strongly influence measured particle concentrations. The TEOM (Tapered Element Oscillating Microbalance) has received significant attention in this area since it uses a heated sample of 50ºC in order to reduce the effects of humidity. This however also causes potential loss of semi-volatile material which means that comparisons between TEOM and other gravimetric measurements show an underestimation of mass by the TEOM [11,12]. An average correction factor of 1.3 has been suggested [13] in order to correct for total PM mass but the percentage of semi-volatile material within a PM10, PM2.5 or PM1 sample may vary with source location, time of day (see later discussion), meteorological conditions or time of year. This makes the use of an average correction factor problematic. In addition, since much of the volatile material is present in the finer fractions, the shift towards PM$_{2.5}$ or PM$_1$ would undoubtedly change the relationship between TEOM and other mass based measurements.

The potential adoption of a number based standard for air quality however, also raises further considerations with regard to the presence of semi-volatile material. High PNC can be dominated by nucleation mode particles. These can be characterised as predominantly droplets of up to 20nm formed in part from semi-volatile gases such as unburnt fuel and lube oil, as well as secondary organics [2,14]. Their formation is highly dependant on atmospheric and dilution conditions as well as pre-existing coarser particle concentrations [15-18]. Another main contributer to high number concentrations in urban areas is the so called Aitken mode (approximately 30 – 100 nm, [2,18]). These are generally internally mixed particles, often with a soot based core and a surface coating of semi-volatiles, potentially including polyaromatic hydrocarbons (PAHs) and other toxic organic and inorganic compounds which may be carried to sites of blood air exchange [19]. The main sources of Aitken mode particles within urban areas are primary exhaust emissions as they are usually associated with incomplete combustion. They are potentially more biologically persistent than nucleation mode particles due to their internally mixed structure. The issue of adopting appropriate metrics for the control of particulate pollutants in order to optimally reduce their impact on the populations’ health is not a straightforward one. This has been acknowledged in Euro VI emissions limit proposals by the suggestion that emissions based measurements should be based on techniques that exclude the volatile...
nucleation mode fraction. Air quality measurements of number concentration do not usually consider such exclusions however. In order to make appropriate decisions regarding particle metrics for air quality, it is first critical that we understand the nature of the particles driving population exposure in terms of particle size, mixing state and composition. This study contributes to improving our understanding by carrying out detailed, high time resolution measurements of size segregated PNCs, as well as particle volatility, at two UK roadside environments. The results serve to highlight the transient nature of exposure to elevated particle concentrations at the roadside, as well as illustrating the complex mixing state of particles in the Uf region.

2. Methodology

2.1. Number concentration study
Short time-scale measurements (1Hz) of PNC and particle size distributions from 4.87<\text{Dp}<1000nm were performed using a Cambustion DMS500 (differential mobility sizer) at a road side location in Leicester, UK. Sampling took place over four weeks during February and March 2005 along a portion of Narborough Road (grid ref. SK 573030) which is an arterial road (A5460) running between Narborough and Leicester with an average bi-directional traffic flow of 1100 vehicles hour$^{-1}$. From a study by Harris et al. [20] this can be expected to be a daytime fleet composition of 88.3% cars, 7.6% LGVs, 1.7% HGVs, 1.7% buses and 0.7% motorcycles, changing to a night fleet composition of 90.7% cars, 7.6% LGVs and 1.7% HGVs. The sampling inlet of the DMS500 was placed at a height of 1.5 m from the ground and 0.3 m from the road. The DMS500 classifies particles based on their mobility in an applied electrical field. A series of grounded electrometer rings situated on the outside of an annular classifier allow simultaneous measurements of distinctly charged particles across multiple size classes, making the DMS500 a fast particulate spectrometer, with a response time of approximately 300 ms allowing near real time measurements [17,21]. Measurements of wind speed (10Hz), solar radiation, traffic detector occupancy (1/4 second) and concentrations of a range of gas phase pollutants (NO, NO$_2$, CO) were also obtained within the study [17]. In addition, in order to investigate the types of vehicles responsible for large peaks in PNC on Narborough Road, video footage was captured for certain periods during the sample campaign so that specific vehicle events responsible for transient increases in particle count could be identified. Such data presented here is from night-time studies since the identification of individual vehicle events is easier due to the more isolated nature of both the transient increases in particle counts and also the isolated vehicles.

2.2. Volatility study
In a subsequent study, 24 hour particle sampling took place on weekdays between July and September, 2007, at a roadside site situated on Kirkstall Rd in Leeds, UK (grid ref. SE 271347). Average bi-directional traffic flow on Kirkstall Rd was found to be 1250 vehicles hour$^{-1}$. Vehicle classification gave an average fleet composition of 89.0% cars, 6.7% LGVs, 1.1% HGVs, 1.6% buses and 1.6% motorcycles. To provide insight into urban particle volatility and mixing state characteristics, measurements of particle size distributions and PNC were performed using a Dekati thermodenuder (TD) in series with the DMS500. In addition, a condensation particle counter (CPC, TSI Model 3025A) and a TSI scanning mobility particle sizer (SMPS, Models 3080, 3085, 3024A) were used to provide reference measurements of PNC and size distributions during the experiments. The SMPS scanned for 4.7<\text{Dp}<160 nm over 210 s, with a down-scan of 20 s leading to a full cycle time of 4 mins. The sample inlet was situated on top of an Air Monitoring Enclosure (AME) approximately 2.8m from the ground and 4.5 m from the road. Full details of the experimental set up can be found in [22]. Eight weeks of sampling took place, including four weeks at ambient temperature and one week each at TD temperatures of 50, 75, 100 and 125°C.
Figure 1. Transient nature of roadside particle counts shown by comparison between 1 second (grey line with black symbols) and 3 minute averages (black line) on Narborough Road, 2nd March 2005.

3. Results

3.1. Calibration study and instrument inter-comparison
Total PNC validation was performed for the DMS500 by the authors using laboratory measurements of urban background air compared with CPC measurements. An SMPS was also tested against the CPC for comparison. The linear relationship between total PNC measured by the DMS (y) and the CPC (x) was \( y = 0.97x \) \((R^2 = 0.82)\), and by the SMPS (y) was \( y = 0.62x \) \((R^2 = 0.52)\), based on a 24 hour diurnal average. This indicates that the DMS500 gives a better representation of the total PNC than the SMPS, perhaps because the latter has longer scanning times causing it to miss potentially important transient increases in concentration. This result alone has implications for the use of number concentrations as a particle standard, since their transient nature means that measured concentrations can be highly dependant on instrument scan times. The high temporal resolution measurements facilitated by the DMS500 help to illustrate this point as discussed below.

3.2. Transient roadside measurements
At the roadside on Narborough Road, particle counts on a second by second basis were often an order of magnitude higher than the 3 minute mean PNCs usually monitored at urban monitoring stations using SMPS instruments as illustrated in figure 1. During certain periods of the day these excursions were found to contribute up to one fifth of total PNC and yet only lasted for a few minutes in total during each hour, as shown in figure 2. Figure 2 also shows diurnal variability in the contribution of these transient peaks to hourly averaged PNC. As expected, peaks in the contribution of transient increases in PNC were seen during rush hour traffic periods (08.00-10.00, 18.00-20.00) but there are also smaller peaks during the night-time (03.00) and in the early afternoon (14.00-15.00) where traffic activity is lower. The exposure of individuals in the roadside environment is regularly dominated by these short term transient peaks, which is often not reflected in toxicological studies [23]. An important question arises as to whether the effects of short term exposure to elevated transient particle concentrations lasting for periods of seconds, are different from those resulting from exposure to the...
same integrated PNC, but over a much longer period of time. Michaels and Kleinman [24] explored the effects in rats of exposure to aerosols with differing degrees of short term excursions from the mean concentration, and found differences in the development of lesions between the two exposure conditions. The excursions in the study were however, 5 minutes long. So far there seem to be no published studies that have examined the effect of shorter transient particle bursts, as have been identified during the current roadside study. The potential importance of such peaks merits further investigation into their sources, and in particular the nature of the size distribution and mixing state of the contributing particles.

Figure 2. Average contribution of 1 s particle counts > 3 x 10^5 cm^-3 (solid line) to total hourly PNC with mean duration per hour of these exceedences (dotted line) over all data for Narborough Road.

Figure 3. Two particle size distributions taken from 4th March 2005, each one a 1 second mean measured at the peak of an elevated number concentration event. Diamonds – nucleation dominated event. Squares – Aitken dominated event.

Figure 3 shows two examples of particle size distributions measured during a peak event. Clearly both have sources of different natures since one is dominated by a burst of nucleation mode particles with a peak around 10nm in diameter, and the other by a burst of Aitken mode particles with a peak diameter of around 42nm. The nature of these particles is potentially different, with the nucleation mode expected to comprise mainly liquid aerosol and the Aitken mode an internally mixed aerosol with a solid core and potentially semi-volatile components absorbed or condensed onto its surface.
This will be further explored in the next section. These particles may have different toxicological implications since the Aitken mode may be more biologically persistent \[25,26\] and therefore it is of interest to explore how each mode contributes to overall particle numbers and peak concentrations. The study of Brauner \[26\] determined that following the exposure of volunteers to ambient particulate concentrations over 6 to 24 hour periods, greater DNA strand breakage was observed after exposure to Uf particles, with the soot mode (57nm) causing the most damage. This soot mode falls within the Aitken mode discussed here.

\[\text{(a) (b)}\]

\[\text{Figure 4. Mean diurnal hourly PNC (solid lines) and } \% \text{ contribution of 1 s exceedences } > 3 \times 10^5 \text{ cm}^{-3} \text{ to hourly PNC (dashed line) of (a) Aitken mode and (b) nucleation mode particles.}\]

The mean modal particle counts for the Aitken and nucleation modes and their \% contribution to peak excursions over \(3 \times 10^5 \text{ cm}^{-3}\) are shown in figure 4. Peak events (1 s PNC\(>3 \times 10^5 \text{ cm}^{-3}\) compared to diurnal means of \(\sim 1 \times 10^5 \text{ cm}^{-3}\)) in the Aitken mode dominate transient PNC increases for most of the day, contributing to a fifth of hourly total PNC during the morning and evening rush hours and during the middle of the day. In contrast nucleation mode events contribute from 7 to 12\% of hourly PNC during the early morning and mid afternoon hours. Higher contributions are seen at night where ambient temperatures and pre-existing Aitken mode particle concentrations are lower, potentially favouring nucleation of semi-volatile gases over condensation onto existing particles \[17,18\].

The domination of the Aitken mode within the transient peak events reflects the transient nature of exhaust emissions. Commonly, it is assumed that the larger, internally mixed Aitken mode particles would be predominantly sourced from diesel vehicles and are soot based in nature. In order to explore this point, particle concentration data and video footage of the concurrent traffic activity passing the sampling site were combined in order to provide a source apportionment of the peaks in particle concentration. Figure 5 shows representative particle size distributions for a series of peak particle concentration events obtained from night-time data 4th March 2005. On the whole, the events associated with the passage of HGVs and LGVs show size distributions typical of the Aitken mode, with count mean diameters (CMDs) in the region of 28-42 nm, although there is also a single large nucleation mode event with number concentrations far in excess of the Aitken mode events. This may relate to rapid cooling and dilution of a diesel exhaust resulting in the saturation ratio of semi-volatile compounds becoming great enough for nuclei formation. Casati et al., \[25\] showed a strong dependence of nucleation mode particle concentrations with dilution temperature and vehicle speeds for a EURO-III diesel passenger vehicle. For passenger cars there are a number of nucleation mode events as well as low numbers of Aitken mode type distributions. This is in broad agreement with previous suggestions that it is diesel vehicles that dominate Aitken mode emissions and that SI engines can produce comparable numbers of particles compared to diesels but with smaller peak diameters \[27\].
The proportion of nucleation mode to Aitken mode particles is highly variable over short timescales and therefore it is worth asking whether a number based standard would adequately reflect the concentrations of the potentially more toxic Aitken mode particles, particularly when a decrease in Aitken mode particles can be accompanied by an increase in nucleation mode numbers. Total PNC measurements do not represent these subtleties. Representative number concentration measurements are difficult to perform and depend strongly on many factors including instrument scan time, transient emissions and dispersion processes, atmospheric temperature and dilution conditions. Total PNC measurements with no size distribution information would not represent the diverse nature of particle sources and their atmospheric processing. Furthermore, whilst the commonly used SMPS gives size distributions, its long scanning time appears to lead to an underestimation of total PNC. In addition, whilst total PNC represents both nucleation and Aitken mode particles, perhaps these two types of particle mixing state are not equally relevant from the toxicological point of view. Nucleation mode particles could be excluded from PNC measurements through absorption or volatilisation techniques but this would have to be achieved consistently and achievable in the roadside environment.

In order to explore the issue of relevant particle measurement metrics, the relationship between nucleation and Aitken mode number concentrations and mass based measurements at the site was explored. Previous roadside studies e.g. [28] have found a poor correlation between PM$_{2.5}$ and Uf number concentrations. However, figure 6a shows that the Aitken mode diurnal hourly average concentrations correlated well with PM$_{2.5}$ at the Narborough Road site, although the nucleation mode did not. This may explain why PM$_{2.5}$ has often been found to be a poor indicator of Uf particle counts, since there is potentially so much variability in nucleation mode concentrations depending on traffic and ambient conditions. However, if PM$_{2.5}$ is adopted as a future standard, the correlation between PM$_{2.5}$ and Aitken mode concentrations may be more important, since these particles are potentially more toxicologically relevant. There have also been suggestions by the scientific community in both Europe and the USA that a PM$_1$ standard would be a better mass standard than PM$_{2.5}$, although a study in the Los Angeles Basin found that complex seasonally dependant relationships existed between PM$_1$ and PM$_{2.5}$ [29]. The potential usefulness of using PM$_1$ as a standard was investigated for the Narborough Road measurements. The mean hourly particle volume between 5 and 1000nm was calculated from size distribution measurements and is used to represent PM$_1$, based on assumptions of sphericity and constant density. The normalised mean hourly Aitken mode PNC plotted against the normalised estimated total volume is shown in figure 6b. Strong correlations ($R^2 = 0.92$) are seen and are stronger than the correlation between PM$_{2.5}$ and normalised Aitken particle count. Given the assumptions made in calculating the particle volume, this is only indicative of the possible relationship that might exist, but shows the potential usefulness of a PM$_1$ standard in representing number concentrations of the potentially more toxic Aitken mode particles. In contrast the $R^2$ value for the equivalent relationship for the nucleation mode is 0.79. The infrastructure change to adopt a PM$_1$
standard would not be too significant, since the measurement would be TEOM based, although the problems associated with the loss of semivolatile material from the TEOM may well be more significant for the lower cut-off size of 1 μm.

(a) Weekday relationship between hourly diurnal average Aitken and nucleation mode PNC and PM$_{2.5}$ on Narborough Road. ■ – Aitken mode ($R^2 = 0.65$), ◊ – nucleation mode ($R^2 = 0.16$). (b) Relationship between normalised diurnally averaged hourly Aitken mode PNC and estimated normalised volume on Narborough Road ($R^2 = 0.92$).

3.3. Further investigation of the nature of nucleation and Aitken modes using volatility studies. Possible differences in particle mixing state between the different size fractions of the whole distribution were suggested in the previous section. This was explored further in a separate study at the Kirkstall Road roadside location in Leeds. Figure 7 represent contour plots of number concentrations across the size distributions for diurnally averaged data across the sampling period for 3 different TD temperatures. Here the concentrations have been adjusted based on simultaneous measurements of total PNC from a CPC in order to account for week to week variability in concentrations. For ambient temperatures it is clear that there are high concentrations across the size distribution from below 10 nm up to 90 nm for much of the day, with particular peaks in the morning rush hour period. The size distributions appear to be continuous with no distinct modes obvious. However, through fitting sums of log normal distributions using the programme R-Mix [30], individual modes can be identified with the hourly diurnal average count mean diameters (CMD) shown on the plots. CMDs of around 10 nm (nucleation mode), 30 nm (small Aitken mode) and 90 nm (larger Aitken mode) are present within the distribution but there is clearly overlap of these modes.

Particular peaks in nucleation mode concentrations are seen during the early morning rush hour and also in the early afternoon (possibly with a secondary aerosol contribution). A distinct peak in the Aitken mode is seen in the morning rush hour. When the sample is heated to 50°C using the TD it is noticeable that the afternoon peak in nucleation mode numbers almost disappears, whilst there is less impact on the morning nucleation mode peak. This suggests that the material contributing to nucleation mode particles in the afternoon is more volatile than that contributing to nucleation mode particles in the morning which might be expected to have primary emission sources from peak traffic numbers. There is a clear drop in nucleation mode numbers in the afternoon following heating to 50°C, indicating that these particles are droplets in nature, possibly comprising semi-volatile alcohols and carbonyl compounds [31]. There are no apparent differences in Aitken mode particle numbers on heating to 50°C, indicating that these are composed of lower volatility components in a possibly internally mixed structure. This is also confirmed by figure 8 where daily average size distributions are presented for the different TD temperatures. The figure includes either normalisation or adjustment of
total number concentrations with respect to total PNC from the CPC measurements in order to account for week to week variability. At 50°C there is a distinct drop in the nucleation mode compared to ambient temperature but no obvious difference for the larger particles.

![Diagram](image1.png)

**Figure 7.** Contour plots of the diurnal variation in number concentration size distributions for diurnally averaged data across the sampling period for (a) ambient temperature (average 14°C), (b) TD = 50°C, (c) TD = 100°C. Also shown is the diurnal variation in hourly average count mean diameter for ● Mode I, □ Mode II, and ▲ Mode III.

Further heating to 100°C leads to a significant change in the diurnal size distribution pattern. Now there is a distinct drop in Aitken mode particle numbers (figure 8) whilst no further reduction in the nucleation mode is observed. This is perhaps surprising since one might expect that further heating would remove further nucleation mode particles of slightly lower volatility than those removed at TD = 50°C. The contour plots of size distribution reveal further interesting features which may help to explain this result. At TD = 100°C (figures 7c,8) distinct modes appear, with peak concentrations more obviously coinciding with the mean CMDs. A possible explanation is that a proportion of the Aitken mode is made up of either agglomerated low volatility particles also incorporating a semi-volatile component, or agglomerated semi-volatiles. On heating, the semi-volatiles are driven off leaving lower volatility particles in the lower size fractions. If these are solid particles, there are potential implications for inhaled particle toxicity, since larger agglomerated particles in the ambient atmosphere could decoagulate, leaving smaller particles that would be classified within the nucleation mode but are not composed of highly volatile droplets. This explanation implies that there is significant coagulation of primary particles in the near field of the exhaust, which is possible given the high concentrations found there during slow moving rush hour periods where initial dispersion due to vehicle movement would be limited. A second explanation is that a proportion of the Aitken mode is comprised of background aerosol which has been processed within the atmosphere and is therefore likely to contain agglomerates. However, in periods of high traffic volume and low traffic speeds the roadside enhancement of PNC is likely to dominate over background sources which would become more significant during night-time periods.
4. Conclusions

High time resolution, size segregated studies of Uf particle number concentrations were performed at two UK roadside locations using a DMS500 particle spectrometer with and without a thermodenuder. Intercomparisons between the DMS500, an SMPS and a CPC, indicate that the SMPS can underestimate total number concentrations compared to the DMS500 and CPC, due to the transient nature of excursions in concentrations and the longer scan time of the instrument. Short time scale periods of high number concentrations were found to make considerable contributions (up to 25% using a threshold of \(3 \times 10^5\) cm\(^{-3}\)) to hourly average total PNC. The duration of these events was often of the order of a few seconds. The transient nature of changes in PNC may have implications for the type of exposure experienced in the roadside environment, as well as for indoor outdoor exchange. It also potentially affects instrument selection for size distributed number concentration measurements.

The transients were dominated by Aitken mode particles during high traffic periods, with the Aitken mode shown to be internally mixed particles with a low volatility core (thought to be primarily soot) and a surface of condensed and absorbed material, some of which was lost on heating with the thermodenuder. Transient periods of high number concentrations of nucleation mode particles were also found, and contributed up to 12% of hourly total number concentrations. They were relatively more important during night-time and afternoon periods, potentially due to secondary formation processes and the lower concentration of pre-existing particles favouring nucleation over condensation or absorption onto existing particles. The TD studies indicated the presence of highly volatile liquid droplets in the nucleation mode which were lost on heating. Such complexities in size distributions and particle mixing state within the Uf fraction, and the discrepancies between instruments, make the potential adoption of a total PNC based standard more complicated than first appears. Numbers of nucleation mode particles are highly dependent on atmospheric conditions such as dilution and temperature as well as pre-existing particle concentrations. They may also be toxicologically less significant if they are predominantly liquid droplets. Although techniques could be developed to remove the nucleation mode from total PNC measurements, their practicality in a roadside environment requires assessment. Aitken mode particles have been shown in previous studies to have relatively high toxicological significance within the Uf fraction [26], and in this study they were seen to dominate the size distribution following heating to >50°C. Their hourly average PNC correlated well with PM\(_{2.5}\) and estimated PM\(_1\), with lower significance of the equivalent correlation of nucleation mode particles. Mass based measurements may easier to undertake on a UK wide basis within existing infrastructure and may well give a reasonable representation of numbers of Aitken mode particles. Issues related to spatial and temporal variability in particle volatility would also affect mass...
measurements however, suggesting further studies of this kind at different types of locations would be useful.

References

[1] Kittelson D B 1998 *J. Aerosol Sci.* 29 575 – 588
[2] Lingard J J N, Agus E L, Young D T, Andrews G E and Tomlin A S 2006 *J. Environ. Monitor.* 8 1203–1218
[3] Ketzel M, Wählin P, Berkowicz R, Palmgreen F 2003 *Atmos. Environ.* 37 2735 – 2749
[4] Oberdörster G, Ferin J, Lehnert B E 1994 *Environ. Health Persp. Suppl.* 102 173 – 179
[5] Anderson HR, Brenner SA, Atkinson RW, et al. 2001, *Occ. Environ. Med.* 58 504-510
[6] de Hartog JJ, Hock G, Peters A, et al., 2003 *Am. J. Epid.* 157 613-623
[7] Kettunen J, Lanki T, Tiittanen P, et al., 2007, *Stoke* 38 918-922
[8] von Klot S, Wolke G, Tuch T, Heinrich J, Dockery DW, Schwartz J, Kreyling WG, Wichmann HE, Peters 2002, *Eur. Resp J.* 20 691-702
[9] Schwartz J, Neas LM, 2000 *Epidemiology* 11 6-10
[10] Osunsanya T, Prescott G, Seaton A, 2001 *Occ. Environ. Med.* 58 154-159
[11] Allen G, Sioutas C, Koutrakis P, Reiss R, Lurmann FW, Roberts PT 1997 *J. Air Waste Man.* 47 682-689
[12] Charron A, Harrison RM, Moocroft S, et al. 2004 *Atmos. Environ.* 38 415-423
[13] Ayers GP, Keywood MD, Gras JL 1999 *Atmos. Environ.* 33 3717-3721
[14] Sakurai H, Tobias H J, Park K, Zarling D, Docherty K S, Kittelson D B, McMurry P H and Ziemann P J 2003 *Atmos. Environ.* 37 1199-1210
[15] Kittelson D B, Watts W F and Johnson J P 2006 *J. Aerosol Sci.* 37 913-930
[16] Shi J P and Harrison R 1999 *Environ. Sci. Technol.* 33 3730-3736
[17] Agus E L, Young D T, Lingard J J N, Smalley R J, Tate J E, Goodman P S and Tomlin A S 2007 *Sci. Tot. Environ.* 386 65-82
[18] Charron A and Harrison R 2003 *Atmos. Environ.* 37 4109-4119
[19] Gerde P, Muggenburg B A, Lundborg M and Dahl A R 2001 *Carcinogenesis* 22 741 – 749.
[20] Harris S, Hodges N, Jenkins H, Ellison J, Bell M C, Goodman P, Namdeo A and Häggkvist K 2003 Project Deliverable 8.11. EU 5th Framework HEAVEN project. Project Ref: IST-1999-11244.
[21] Cambustion 2005 DMS500 Fast Particulate Spectrometer, User Manual. Cambustion, Cambridge.
[22] Agus E L, Lingard J J N, Andrews G E, Tate J E, Ropkins C and Tomlin A S 2008 Using volatility analysis to investigate aerosol processing in a roadside environment, in prep.
[23] Oberdörster G, Oberdörster E and Oberdörster J 2005 *Environ. Health Persp.* 113 823-839
[24] Michaels R A and Kleinman M T 2000 *Aerosol Sci. and Technol.* 32 93-105
[25] Casati R, Scheer V, Vogt R and Benter T 2007 *Atmos. Environ.* 41 2125-2135
[26] Bräuner E V, Forchhammer L, Moller P, Simonsen J, Glasius M, Wählin P, Raaschou-Nielsen O and Loft S 2007 *Environ. Health Persp.* 115 1177-1182
[27] Kittelson D B, Watts W F, Johnson J P, Schauer J J and Lawson D R 2006 *J. Aerosol Sci.* 37 931-949
[28] Molnar P, Janhill S and Hallquist M 2002 *Atmos. Environ.* 36 4115-4123
[29] Geller M D, Fine P M and Sioutas C 2004 *J. Air & Waste Man. Assoc.* 54 1029-1039
[30] Leys J, McTanish G, Koen T, Mooney B and Strong C 2005 *Earth Surface Processes and Landforms* 30 579-590
[31] Ning Z, Geller M D, Moore K F, Sheesley R, Schauer J J, Sioutas C, 2007. *Environ. Sci. Technol.* 41 6000 – 6006