6.5 Particle number: concentrations and size distributions

6.5.1 Particle number concentrations

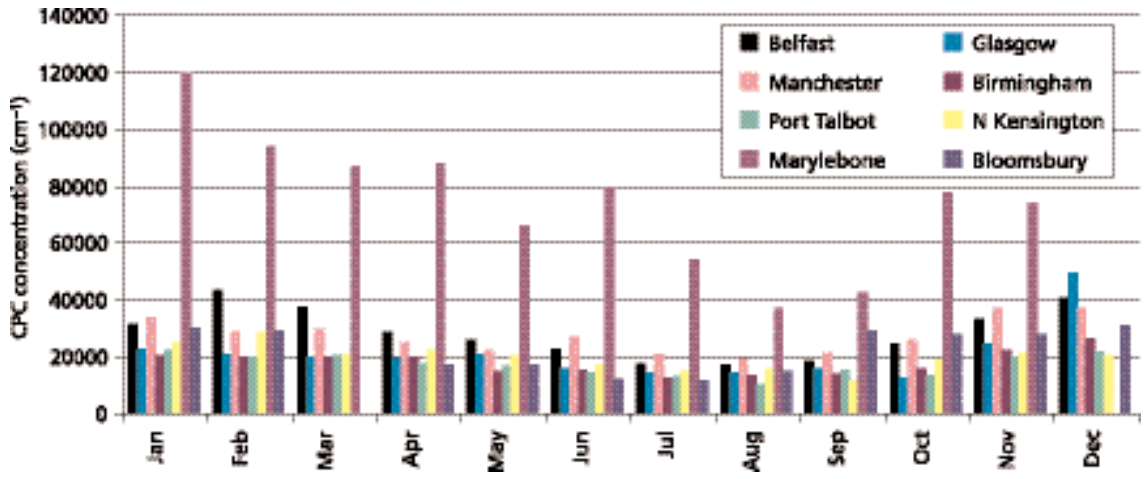
669. Particle number concentrations have been measured using TSI model 3022A Condensation Particle Counters at eight sites. This instrument measures the number of particles in the size range of ~7 to 2000 nm. Data are collated over 15-min periods. Seven instruments were progressively introduced from early 2000 with one instrument being located at Marylebone Road up until March 2002 and then transferred to Bloomsbury. The sites used, their type and location, and the periods of instrument operation are presented in Table 6.21.

Table 6.21 Operating sites of CPC instruments.

Site	Type of site	OS location	Operating period
Belfast centre	Urban centre	J 339744	Jan 2000 – present
Glasgow centre	Urban centre	NS 589650	Feb 2001 – present
Manchester Piccadilly	Urban centre	SJ 843983	Jun 2000 – present
Birmingham centre	Urban centre	SP 064868	Feb 2000 – present
Port Talbot	Urban background	SS 780882	Jan 2000 – present
North Kensington	Urban background	TQ 240817	Apr 2000 – present
Marylebone Road	Kerbside	TQ 281820	Jan 2001 – Mar 2002
London Bloomsbury	Urban centre	TQ 302820	Apr 2002 – present

670. The monthly means of particle number concentration at each of the sites are shown in Figure 6.119. No data were collected at the Marylebone Road or Bloomsbury sites during the months of December and March, respectively, due to operational reasons. The data for all sites show the same general trend with minimum concentrations occurring during the summer months and higher concentrations during the winter. Concentrations measured at the Marylebone Road (kerbside) site are substantially greater that those measured at the other sites.

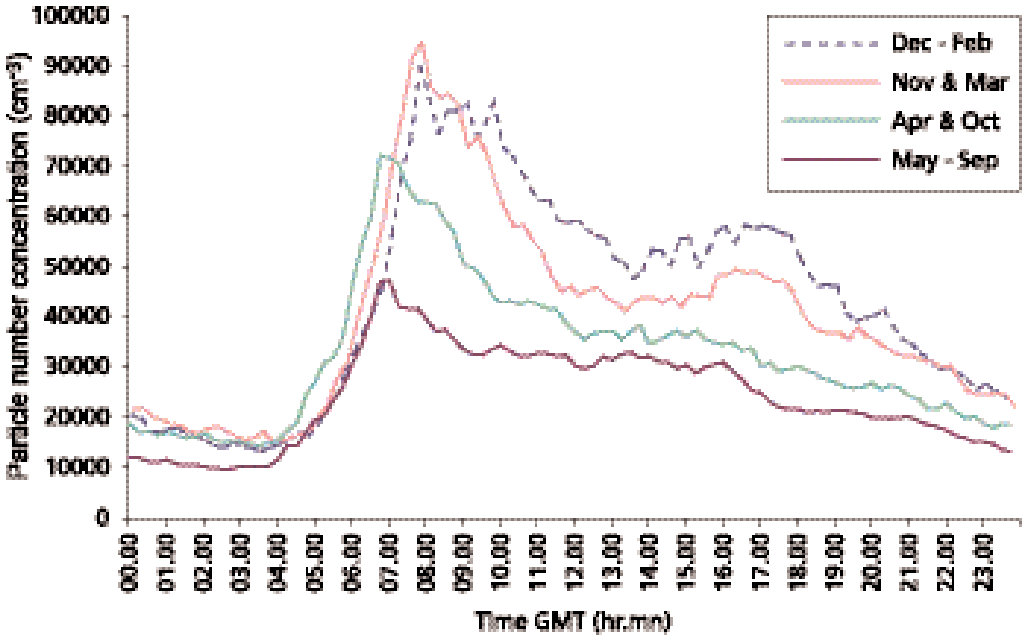
Figure 6.119 Monthly mean particle number concentration at eight sites 2000–2003.



671. Diurnal profiles of particle number concentration were similar to those of particle mass measured in urban areas with peak concentrations occurring around the morning commuting period and some evidence of a secondary peak during the

evening commuting period. Diurnal profiles of particle number concentration obtained during weekdays (Monday to Friday) in Belfast during 2002 are shown in Figure 6.120. The data are divided into four groups consisting of the months before and after the changes of clock time on, respectively, the 31 March and 27 October (March and November – including 28 to 31 October); the months after and before these changes of clock time (April and October – excluding 28 to 31 October); the winter months; and the remaining spring and summer months. The 15-min time base of the data makes it possible to distinguish the earlier peak in concentrations at 06:45 GMT, rather than 07:45 GMT, when clock times are brought forward during the summer. The summer trend of lower particulate number concentrations seen in Figure 6.119 is also evident in Figure 6.120. Little evidence of a morning peak in concentration was seen in data collected on Sundays.

Figure 6.120 Diurnal weekday CPC profiles, Belfast 2002.



672. Particle number concentration data (CPC) and concurrently measured PM_{10} and NO_X data collected during 2000–2002 were separated by wind direction data provided by the British Atmospheric Data Centre for a nearby meteorological station. To allow comparison between the different pollutants, the normalised mean concentration for each wind direction was plotted against wind direction. The results for Birmingham are shown in Figure 6.121: the inner circle represents the mean concentration over all directions and the outer circle represents twice the mean. Meteorological data for Birmingham are from Elmdon (Birmingham Airport),12 km to the east of the Birmingham centre air quality measurement site. Figure 6.121 shows a strong peak at 110° from the measurement site with the normalised concentration of particle number at this direction increasing by a greater amount than the increase in normalised PM_{10} concentration, but by a lesser amount than the increases in the normalised NO_X concentration. There may also be some increase in the normalised concentrations in the 30°–40° and 130–140° directions. The major peak at 110° may be associated with local sources in the city centre or with longer range sources.

Figure 6.121 Birmingham normalised concentration versus wind direction.

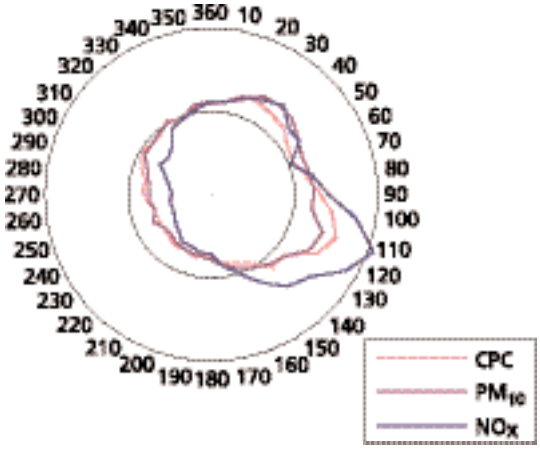


Figure 6.122 Port Talbot normalised concentration versus wind direction.

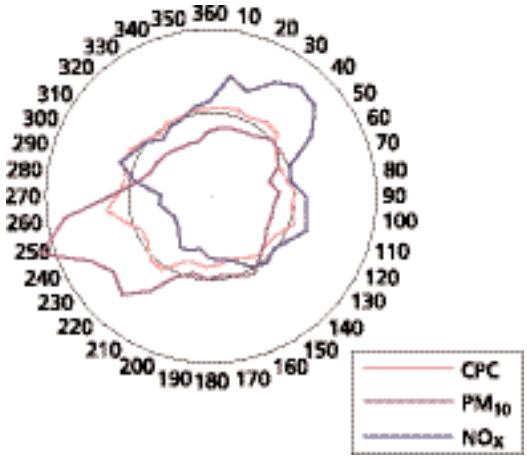
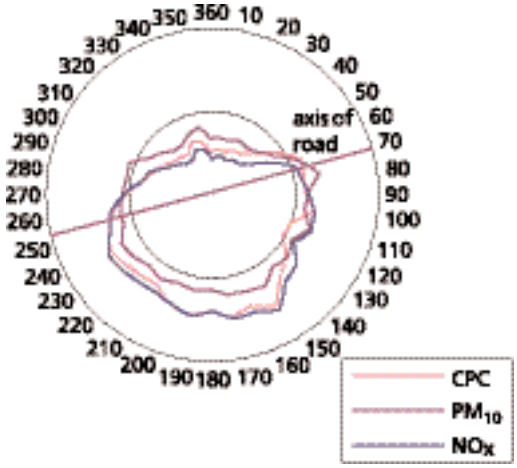


Figure 6.123 Marylebone Road normalised concentration v wind direction.



673. The normalised particle number (CPC), PM_{10} and NO_X concentration data for Port Talbot are plotted against wind direction in Figure 6.122. In this case meteorological data are from Mumbles Head, 15 km to the west. There is little variation in the normalised particle number concentration unlike the raised levels of NO_X when the wind is from the northeast or the raised levels of PM_{10} when the wind is from the west-southwest. The raised levels of NO_X can be associated with the M4 motorway carrying 50,000 to 55,000 vehicles on a typical weekday, 75 m away to the northeast. The raised levels of PM_{10} can be associated with a large steel works that is ~700 m away to the west and south and is a likely source of larger fugitive dust, which will affect the measure of PM_{10} more than it does particle number (see also Section 6.4.9).

674. Figure 6.123 shows the normalised particle number (CPC), PM_{10} and NO_X concentrations measured at Marylebone Road plotted against wind direction. Wind data are from Heathrow Airport 23 km to the west-southwest of the site. The Marylebone Road sampling site is on the southern kerb of the road, which is aligned on an axis of 75°–255°, within a street canyon, with buildings of a height similar to the distance between buildings on either side of the street. The normalised concentrations of all pollutants are higher when the wind is from southerly directions under which conditions the airflow crossing the top of the

street canyon can be expected to induce an opposite flow at street level. Two patterns of normalised pollutant distribution are evident in Figure 6.123. The normalised PM_{10} concentration is similar at all directions when the wind direction is from the south side of the street. The normalised concentrations of particle number and NO_X show higher concentrations when the wind is between 150–250° than when the wind direction is between 80–140°. These two patterns of distribution are apparent for other pollutants, with carbon monoxide and elemental carbon following the NO_X distribution and $PM_{2.5}$ and organic carbon following the PM_{10} distribution. There is a major road junction to the west of the sampling site and it may be that stationary traffic queuing to pass through this junction produces greater quantities of certain pollutants.

6.5.2 Particle number size distributions at a rural (Harwell), urban (Bloomsbury) and roadside (Marylebone Road) sites

675. Datasets from February and March 2002 for Harwell, Bloomsbury and Marylebone Road have been analysed and appear in Figures 6.124–6.126.

Figure 6.124 Median particle number size distributions for the period February to March 2002 at the three sites.

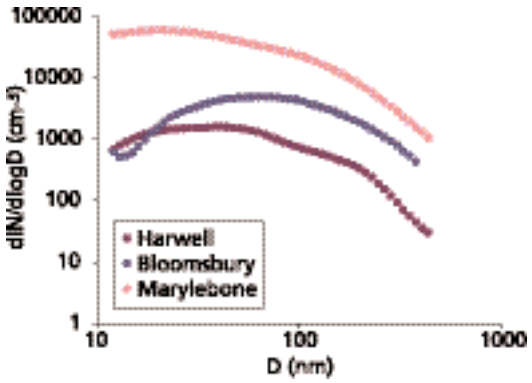
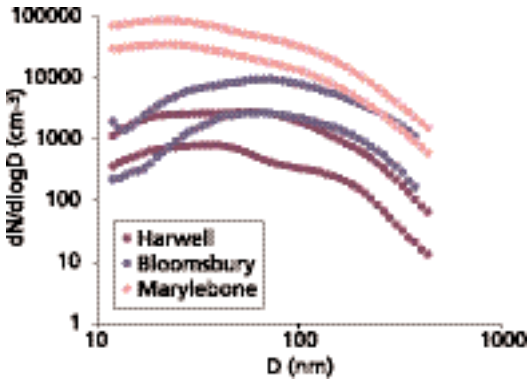


Figure 6.125 The 25 and 75 percentiles of particle number size distributions for the period February to March 2002 at the three sites.



676. The median number size distributions measured at the three sites are so different that the better scale to represent $\partial N/\partial \log D$ is a logarithmic scale (Figure 6.124). As expected, particle numbers are higher at the Marylebone Road site, strongly influenced by on-road emissions that have a large impact on particle numbers and higher at the urban background of Bloomsbury than Harwell.

677. The difference between numbers of particles below 100 nm is larger between the roadside site and the urban background than between the urban background and the rural site. Additionally, median normalised particle counts of particles below 20 nm at Harwell are higher than those measured at Bloomsbury. This suggests that dilution of urban vehicular sources is not the only reason for differences between sites. There are actually two explanations for this. Firstly, freshly emitted particles below 100 nm have a short lifetime in the atmosphere due to coagulation and other processes. Their number rapidly drops with the distance from the road. New particle formation at Harwell is occasionally responsible for high concentrations of very small particles (see Section 6.5.5).

678. In comparison, for particles above 300 nm the difference between the roadside site and the urban background is smaller than the difference between the urban background and the rural site.

679. Marylebone Road shows considerably higher concentrations than the other sites. The difference is larger for particles below 100 nm and very large for particles below 40 nm. The difference reaches a factor of about 100 for particles below 20 nm. This confirms that on-road vehicle emissions are a very important source of particles and especially of very small particles.

680. The difference between median particle number size distributions at Bloomsbury and Harwell is quite constant for particles above 70 nm; but is weaker and weaker for particles below 70 nm, and median normalised numbers of particles below 20 nm are higher at Harwell than at Bloomsbury. This is probably the consequence of new particle formation at Harwell responsible for occasional bursts of small particles while new particle formation at Bloomsbury is probably very limited because of the large pre-existing particle surface area that prevents homogenous nucleation.

681. Examination of the median particle number size distributions for different periods of the days does not show any considerable difference indicating that the intra-site variability is much lower than the inter-site variability (Figure 6.126).

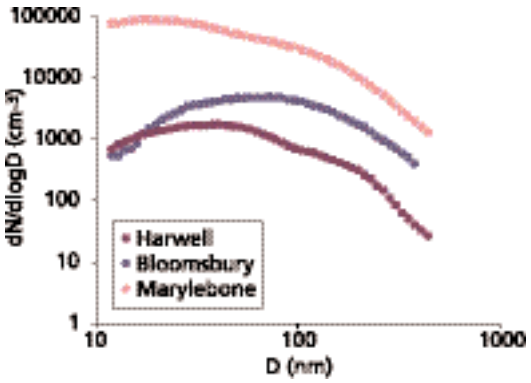
682. Figure 6.125 presents the 25 and 75 percentiles of the particle number size distributions: 50% of the particle number size distributions measured are between these two series of values. This indicates the spread of particle number size distributions.

683. The 25th percentile of the particle number size distribution at Marylebone Rd and the 75th percentile of the particle number size distribution at Bloomsbury show similar normalised counts of particles above 300 nm. This shows that within the >300 nm size range, the less polluted conditions at Marylebone Road are not dissimilar to the more polluted at Bloomsbury, despite the large differences under average conditions.

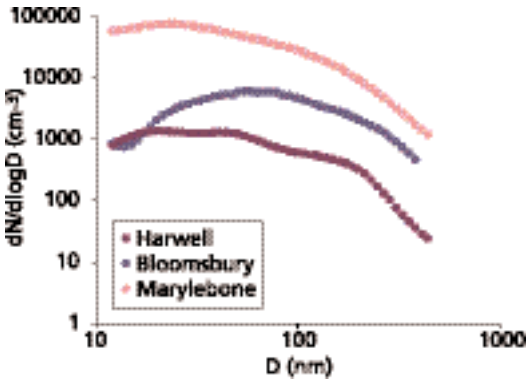
684. The 25th percentile of the particle number size distribution for Bloomsbury and the 75th percentile of the particle number size distribution for Harwell show similar normalised counts of particles above 50 nm, while there is almost a factor 10 between the two sites for particles below 50 nm. This shows that the most polluted conditions at Harwell are similar to the less polluted conditions at Bloomsbury, except for small particles.

Figure 6.126 Median particle number size distributions for the period February to March 2002 at the three sites as a function of the time of the day.

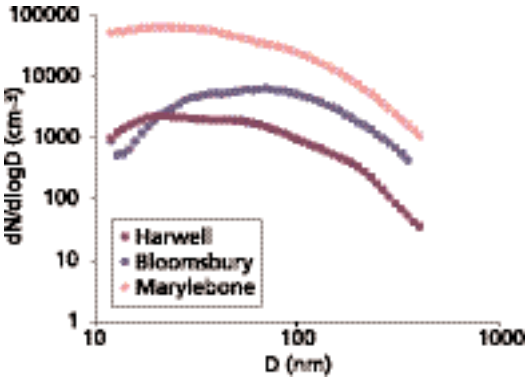
(a) Mornings (05:00–10:00 h)



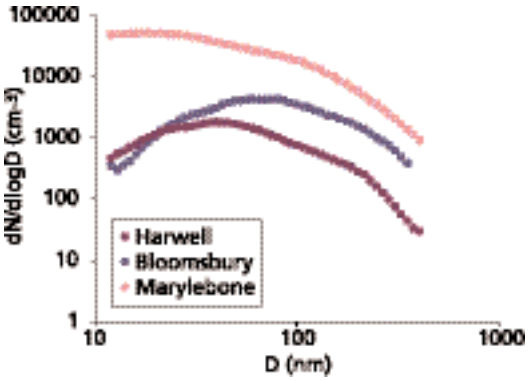
(b) Midday period (11:00–16:00 h)



(c) Evenings (17:00–21:00 h)



(d) Nights (22:00–04:00 h)



6.5.3 Particle formation from vehicle emissions at Marylebone Road

685. In contrast to the other particle size ranges and to the particle mass ($PM_{2.5}$, PM_{coarse}), the numbers of the smallest particles (below about 30 nm) are not strongly correlated with the traffic intensity. The highest concentrations of the smallest particles occur in the morning of the weekdays and during the Friday to Saturday and Saturday to Sunday nights of the weekend (Figures 6.127 and 6.128). This corresponds to the beginning of the morning rush hour of weekdays and, at the weekend, to intense leisure traffic during the night. Interestingly, during the weekdays, the decrease of the particle number from the morning rush hour to the afternoon rush hour is associated to a simultaneous shift of the mode of the particle size distribution from ~23 nm to ~31 nm as well as an increase of the mean diameter of ultrafine particles (11–100 nm) from 35–39 nm.

686. Another particular feature of these very small particles is their unusual behaviour with meteorological parameters. Wind speed does not seem to influence their concentrations, whereas an increase of wind speed significantly reduces the concentrations of the other particle fractions. Also worthy of note, the wind speed generates a shift of the size distribution to finer diameters and an increase of the relative number (Figure 6.129). Rain events are associated with higher particle numbers and drought periods are associated with much lower particle numbers. In addition, particle mass increases with the duration of the drought period due to accumulation in the atmosphere in the absence of washout.

Figure 6.127 Weekly median cycles of integrated particle numbers from 11 to 30 nm, particle surface area, heavy duty traffic and light duty traffic.

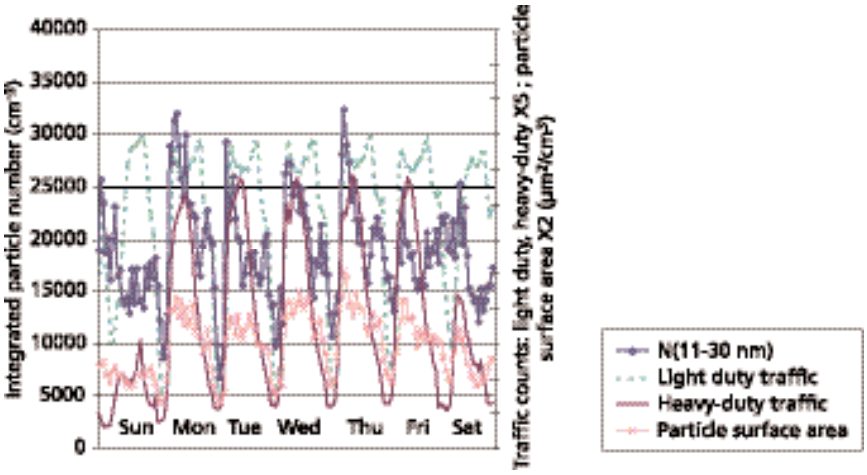


Figure 6.128 Weekly median cycles of integrated particle numbers from 30 to 100 nm and from 100 to 450 nm, heavy duty traffic and light duty traffic.

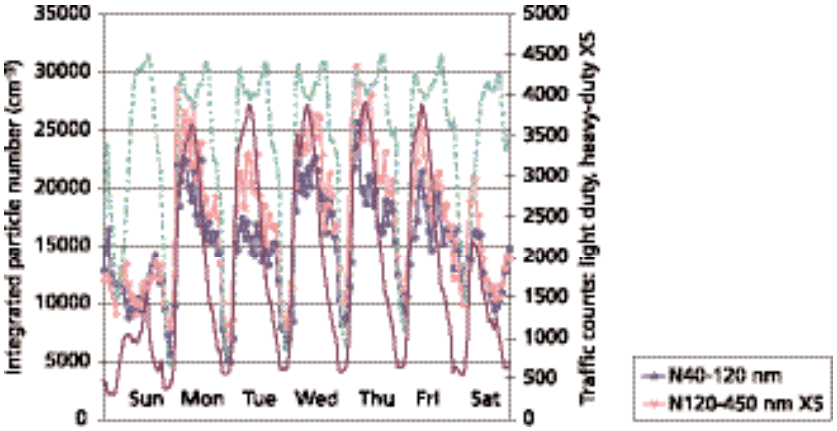
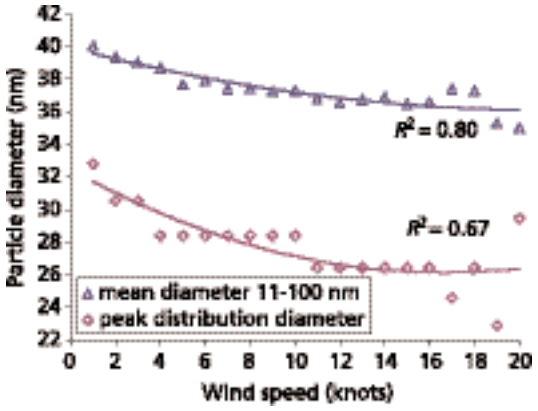
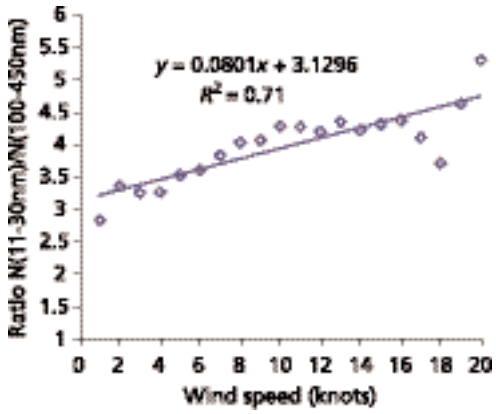


Figure 6.129 Relation between wind speed and (a) the particle diameters (b) the ratio of integrated particle counts from 11 to 30 nm to integrated particle counts from 100 to 450 nm.

(a)



(b)



687. These observations clearly indicate that some factors favour the occurrence of the small particles in the early morning and during the night. They also suggest that 'cleaner atmospheres' created by stronger winds and rain events favour the occurrence of high numbers of ultrafine particles. This suggests that these

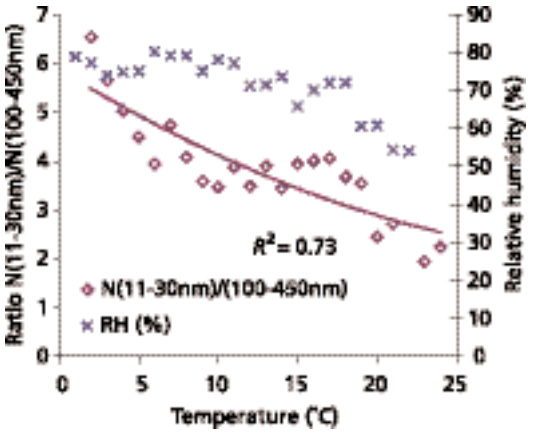
particles are not directly emitted by motor vehicles but formed during the cooling and dilution of vehicle exhaust in the atmosphere of Marylebone Road. On the other hand, the evolution of the particle diameter and the lower number of ultrafine particles during the midday and the afternoon suggests that the high on-road emissions lead mainly to the growth of particles via condensation processes that would be more favourable than new particle formation during these parts of the day. The possible coagulation of the small particles formed in the early morning is also in agreement with the evolution of both particle diameters and numbers.

688. After dilution in the atmosphere, the exhaust gases are cooled and diluted; the saturation ratio of gaseous compounds of low volatility reaches a maximum. Then, two major processes are possible: firstly, the nucleation and formation of new particles, and secondly, condensation onto existing particles.
The occurrence of these two processes will depend on the particle surface area available for the condensation of the semi-volatile species. Small pre-existing aerosol concentrations favour both the production of new particles and their growth to detectable sizes in the atmosphere (Kulmala *et al*., 2000). In contrast, high concentrations of pre-existing particles both promote the condensation of the semi-volatile vapours and disfavour the growth of fresh nuclei and their survival from high coagulational scavenging (Kerminen *et al*., 2001). The large amounts of semi-volatile vapours from vehicle exhausts in the early morning, associated with low pre-existing particle surface area (~300–500 $\mu m^2 cm^{-3}$), would favour both production of new particles and their growth to detectable sizes (>11 nm). During daytime, when the particle surface area ranges from 800 to 1100 $\mu m^2 cm^{-3}$, condensation of the emitted condensable gases onto existing particles is likely to be the most favourable process.

689. The mixing of two air parcels with different temperature and different relative humidities increases nucleation rates significantly (Nilsson and Kulmala, 1998) and this is comparable with the mixing of hot exhaust vapours with cool air. More efficient mixing (by a stronger wind) with colder air is, therefore, expected to improve nucleation rates. More efficient mixing by stronger winds would also lessen the possibility of particle coagulation and new particle self-coagulation, which would in turn have an impact on their diameters.

690. Some meteorological parameters such as low temperatures and high relative humidity favour the formation of new particles (Easter and Peters, 1994).
In the morning and during the night the temperature is lower and the relative humidity higher. The relative number of particles ranging from 11 to 30 nm measured during the morning rush hour is strongly influenced by the temperature (Figure 6.130). Lower temperature favours the relative number of small particles (ratio to the other size ranges). This strong dependence on the temperature is further support for the idea that these particles are not a primary emission but are formed during the cooling and dilution of the vehicle exhaust. In contrast, no obvious relation has been found with relative humidity despite the diurnal anti-correlation of temperature and relative humidity. Higher water contents in the atmosphere are expected to favour homogeneous binary nucleation of sulphuric acid and water (Easter and Peters, 1994), whereas ternary nucleation involving ammonia is expected to be independent of relative humidity (Korhonen *et al*., 1999), and the possible nucleation from organic compounds might not be influenced by relative humidity.

Figure 6.130 Relation between the temperature and the ratio of integrated particle counts from 11 to 30 nm to integrated particle counts from 100 to 450 nm and the relation between the relative humidity and the temperature.

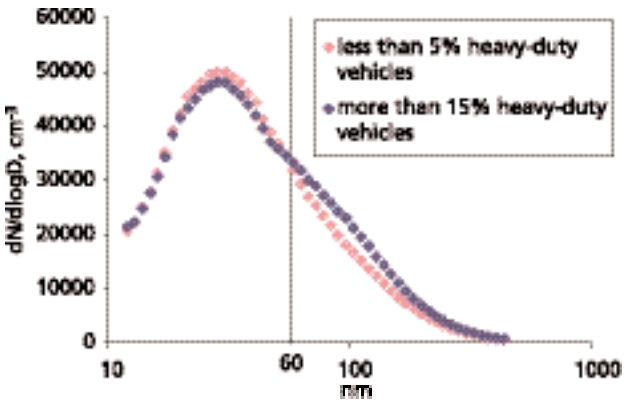


6.5.4 NanoSMPS data at Marylebone Road

691. Measurement data from 25 September 2003 to 18 November 2003, comprising 7,767 10-min particle number size distributions ranging from 5 to 184 nm, have been analysed using a nanoSMPS, which measures smaller particle sizes than in the earlier work.

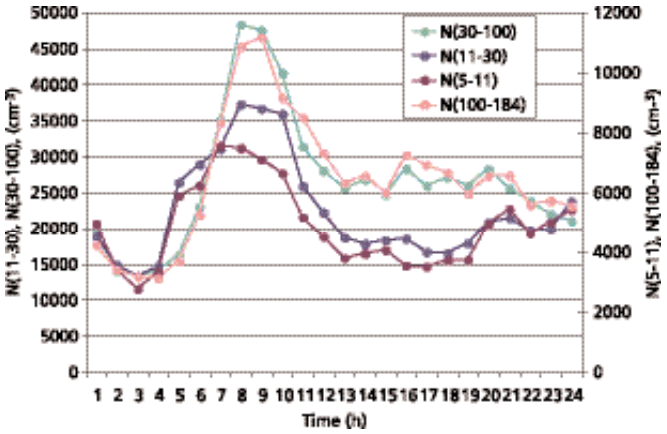
692. The peaks in the size distributions range from 20 nm to 30 nm, which is in good agreement with the previous work and other roadside studies. Another mode around 60–80 nm seems to be hidden by the largest mode around 25 nm. This is apparent in earlier measurements only when the proportion of heavy duty vehicles exceeds 15% (Figure 6.131).

Figure 6.131 The 1998 to 2000 average size distributions from Marylebone Road SMPS data.



693. The pattern observed on Figure 6.132 confirms that particles below 11 nm are from vehicle emissions (the same figures for the weekends are not presented because of the small datasets). The daily cycle of particles ranging from 5 to 11 nm is quite similar to that for particles ranging from 11 to 30 nm. On the other hand, particles ranging from 30 to 100 nm and particles ranging from 100 to 181 nm show similar patterns to one another. Concentrations of the former increase from 03:00 h to reach their maxima at 07:00 to 08:00 h and then decrease from 10:00 to 18:00 h. Then, concentrations of both particles ranging

Figure 6.132 Median daily integrated particle numbers for weekdays.



from 5 to 11 nm and particles ranging from 11 to 30 nm increase slightly to reach a second maximum around 22:00 h. Larger particles (above 30 nm) do not show this second maximum (their concentrations decrease from the morning to the night) and, additionally, a shift between particles below 30 nm and above 30 nm can be seen in the morning.

694. In agreement with earlier work, during weekdays, the decrease of the total particle number from the morning rush hour to the afternoon rush hour is associated with a simultaneous shift of the mode of the particle size distribution from about 21 nm to about 35 nm as well as an increase in the median diameter from 26 nm to 37 nm.

6.5.5 Homogenous nucleation events at Harwell

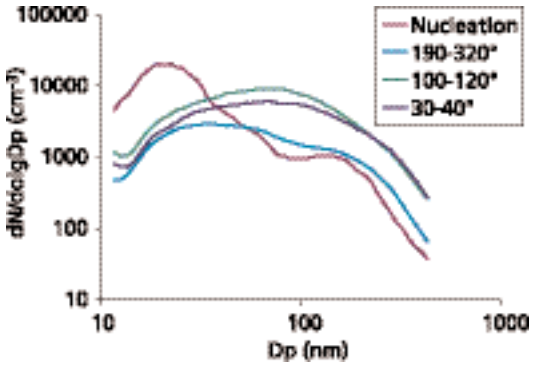
695. The term homogenous nucleation refers to the process of gases condensing to form wholly new particles.

696. High particle number concentrations at Harwell are often associated with plumes from the nearby A34 road (about 100° to 120° direction). Few events involving significant particle numbers that can be attributed to photochemically induced homogenous nucleation events are observed at the Harwell rural site. Observed particle number size distributions suggest that most events may have occurred upwind of the Harwell site. All events occurred during the warm period of the year.

697. Figure 6.133 represents median particle number size distributions corresponding to four different situations at Harwell: (i) possible homogenous nucleation events that occurred in 2000; (ii) winds blowing from 100°–120° directions, that is, downwind of the closest part of the A34 road, 2 km away; (iii) winds blowing from 190°–320° directions, that is, clean air masses; (iv) winds blowing from 30°–40° directions, that is, downwind of Didcot power station (with a possible influence of traffic).

698. The Aitken mode generally dominates at Harwell: the highest numbers are generally measured within the 30–100 nm particle diameter range. Similar median total integrated particle numbers (11–450nm range) are observed for the A34 traffic influence and during (or downwind) events of homogenous nucleation

Figure 6.133 Four median particle number size distributions at Harwell: for homogenous nucleation events (midday hours) and for certain wind directions: 30°– 40° (Didcot power station + possible influence of traffic); 100–120° (the closest parts of the A34 road); 190–320° (clean air masses conditions). Log-log scale.

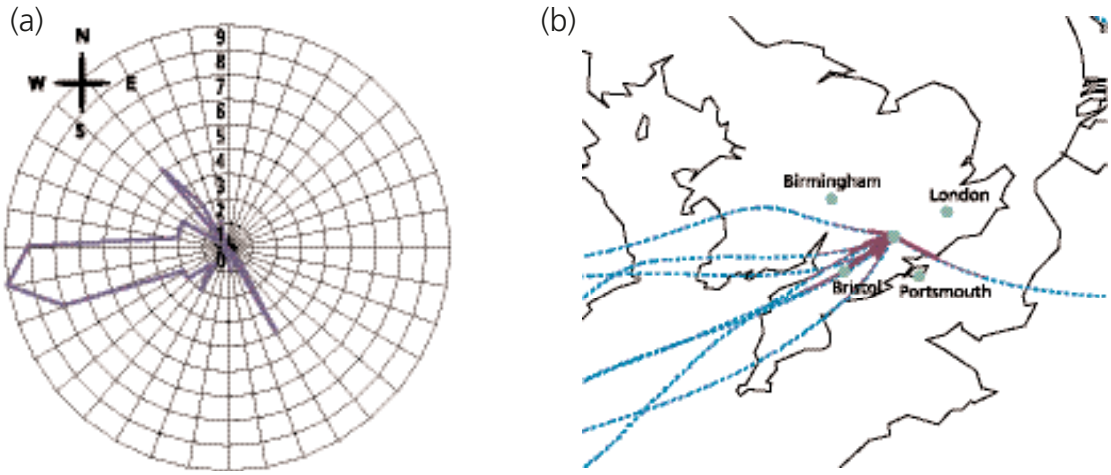


(medians of about 7000 cm^{-3}). However, very different particle number size distributions are measured. The median particle size distribution for homogenous nucleation events shows two modes: one around 20 nm and another one above 100 nm. The median particle number size distributions for anthropogenic influences (from the A34 road and from the Didcot power station) show one single large mode around 70 nm. The one for clean conditions shows a mode around 35 nm and a second mode above 100 nm. In such clean conditions, particle number size distributions were generally bimodal or trimodal.

699. The events of homogeneous nucleation that occurred at Harwell in 2000 have been examined. New particle formation events occurred on cleaner days and especially the most spectacular bursts of particles (days with lower particle surface area, lower concentrations of particles ranging from 100 to 450 nm and lower concentrations of pre-existing particles ranging from 30 to 100 nm). The influence of the particle surface area is consistent with competition between homogeneous nucleation and condensation of vapour onto existing particles. Both the formation and the growth of new particles are favoured by small pre-existing aerosol concentrations, whereas high particle surface areas promote the condensation of the semi-volatile vapours and disfavour the survival of new nuclei from coagulation scavenging (Kulmala *et al*., 2000 ; Kerminen *et al*., 2001). A low particle surface area is possibly not the only influential parameter since high particle surface areas were measured on days of nucleation events at other sites (Harrison *et al*., 2000; Birmili and Wiedensohler, 2000).

700. The examination of wind direction and backward trajectories shows that in 2000, new particle formation often occurred when winds blew from westerly directions, bringing clean air masses from the northern Atlantic Ocean over rural areas, except 18th June (see Figure 6.134). Conversely, easterly winds are generally associated with higher particle numbers at Harwell, in consistent with the location of most of the local anthropogenic sources (the A34 road and London to the east-southeast; Didcot and Didcot power station to the northeast). Table 6.23 shows that the weather is significantly better on days of homogeneous nucleation. Events of homogenous nucleation occurred on days with higher global daily insolation and low cloud cover. In common with the Melpitz site (Eastern Germany; Birmili, 1999), these days had also lower relative humidity, slightly higher temperature and higher winds speeds.

Figure 6.134 (a) Wind direction associated with nucleation events in the year 2000 (in number of hours per direction). (b) Possible pathways of air masses associated with nucleation events and possible areas where nucleation had occurred upwind of Harwell. Backward trajectories end at noon at Harwell (from the British Atmospheric Data Centre).



701. Mode diameters generally observed at Harwell suggest that events of homogenous nucleation had possibly occurred upwind of the Harwell site. Figure 6.134b represents the possible pathways of air masses coming to Harwell on days of nucleation and the possible areas where nucleation had occurred. The possible positions where nucleation had occurred are highlighted on the figures in red (assuming a minimum growth rate of 4 nm/h) and in bold red (assuming a minimum growth rate of 10 nm/h). The length of the highlighted pathways also depends on the wind speed and on mode diameters observed at Harwell and assumes that newly formed particles have grown from about 1 nm initial diameter.

Table 6.23 Median values for nucleation events in the year 2000. Particle surface area (PSA) in $\mu m_2/cm_3$, integrated particle numbers for the 11–30, 30–100, 100–450 nm ranges in cm^{-3}; O_3, SO_2, and NO_X in ppb, wind speed (WS) in knots (0.515 m s^{-1}), total cloud amount (TCA) in Oktas (0,1,2: fine; 3,4,5: fair; 6,7,8: cloudy), T in °C, RH in %, global irradiation amount (GIA) in kJ m^{-2}. For the SO_2, zero concentration is assumed below the detection limit (DL) of the instrument.

	PSA	11-30 nm	30-100 nm	100-450 nm	O_3	SO_2	NO_X	WS	TCA	T	RH	GIA
Nucleation	61	6556	1977	345	39	1	2	11	3: fair	15.6	53	20,300
All data, midday time	103	878	1898	761	32	1	6	9	7: cloudy	14.0	68	10,300
All data	112	716	2118	818	27	< DL	6	7	7: cloudy	11.1	84	10,300