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# Remarkable dynamics of nanoparticles in the urban atmosphere

**M. Dall'Osto<sup>1,\*</sup>, A. Thorpe<sup>1</sup>, D. C. S. Beddows<sup>1</sup>, R. M. Harrison<sup>1</sup>, J. F. Barlow<sup>2</sup>, T. Dunbar<sup>2</sup>, P. I. Williams<sup>3</sup>, and H. Coe<sup>3</sup>**

<sup>1</sup>National Centre for Atmospheric Science Division of Environmental Health and Risk Management School of Geography, Earth and Environmental Sciences University of Birmingham, Edgbaston, Birmingham, UK

<sup>2</sup>Department of Meteorology The University of Reading, Earley Gate, P.O. Box 243, Reading Berkshire, RG6, 6BB, UK

<sup>3</sup>National Centre for Atmospheric Science School of Earth, Atmospheric and Environmental Sciences The University of Manchester, Williamson Building, Oxford Road Manchester M13 9PL, UK

\*now at: Institute of Environmental Assessment and Water Research, Spanish Research Council (IDEA-CSIC), c/Jordi Girona 18-26, 08034 Barcelona, Spain

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Correspondence to: R. M. Harrison (r.m.harrison@bham.ac.uk)

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## Abstract

Nanoparticles emitted from road traffic are the largest source of respiratory exposure for the general public living in urban areas. It has been suggested that the adverse health effects of airborne particles may scale with the airborne particle number, which if correct, focuses attention on the nanoparticle (less than 100 nm) size range which dominates the number count in urban areas. Urban measurements of particle size distributions have tended to show a broadly similar pattern dominated by a mode centred on 20–30 nm diameter particles emitted by diesel engine exhaust. In this paper we report the results of measurements of particle number concentration and size distribution made in a major London park as well as on the BT Tower, 160 m high. These measurements taken during the REPARTEE project (Regents Park and BT Tower experiment) show a remarkable shift in particle size distributions with major losses of the smallest particle class as particles are advected away from the traffic source. In the Park, the traffic related mode at 20–30 nm diameter is much reduced with a new mode at <10 nm. Size distribution measurements also revealed higher number concentrations of sub-50 nm particles at the BT Tower during days affected by higher turbulence as determined by Doppler Lidar measurements and indicate a loss of nanoparticles from air aged during less turbulent conditions. These results suggest that nanoparticles are lost by evaporation, rather than coagulation processes. The results have major implications for understanding the impacts of traffic-generated particulate matter on human health.

## 1 Introduction

Urban air pollution is one of the environmental problems of major concern and, due to growing urbanization, will probably become increasingly important in the future. Particulate matter is one of the key urban pollutants and much attention has focussed on the smaller size fractions. Ultrafine particles (UF) are defined as those with diameters

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smaller than 0.1  $\mu\text{m}$  (100 nm), and nanoparticles as particles with one dimension smaller than 100 nm. The size of airborne particles is heavily influenced by the multiplicity of sources and processes leading to their emission and formation, and thus, by the material from which the particles were formed. The interest in UF particles has resulted in a large body of literature published in recent years, reporting on various aspects and characteristics of these particles (Morawska et al., 2008). Within the urban environment, the most significant sources of UF are various outdoor anthropogenic combustion sources, including vehicles (and other forms of transport), as well as industrial and power plants utilising fossil fuels (AQEG, 2005). Once the particles are emitted, they are quickly modified by a number of physical and chemical processes, of which knowledge remains incomplete. Current regulations address the amount of ambient particulate matter (PM) as PM<sub>10</sub> ( $D_p \leq 10 \mu\text{m}$ ) and PM<sub>2.5</sub> ( $D_p \leq 2.5 \mu\text{m}$ ) expressed as a mass concentration of particles, and not particle number concentrations. It has been shown that in urban environments, the smallest particles make the highest contribution to the total particle number concentrations, but only a small contribution to particle volume or mass (Harrison et al., 2000). Recent toxicological studies have suggested that ultrafine particles, i.e., the fraction of fine particles below 100 nm and the main component of ambient particles by number, are more toxic than coarser particles, per unit mass (Davidson et al., 2005; Seaton et al., 1995) and a recent epidemiological study in London (Atkinson et al., 2010) showed a strong association between particle number concentrations and both cardiovascular mortality and hospital admissions. Particles from road vehicles arise either from exhaust or from abrasion sources such as the wear of brakes, tyres and the road surface.

In general, particles from vehicle exhaust can be divided into two broad categories, depending on where they are formed. They can be formed in the engine or in the atmosphere following emission from the tailpipe (Shi and Harrison, 1999; Charron and Harrison, 2003). Particles formed within the engine are mostly submicrometre agglomerates of solid phase carbonaceous material ranging in size from 30 to 500 nm and residing mainly in the accumulation mode. They may also contain metallic ash and

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adsorbed or condensed hydrocarbons and sulphur compounds (Schelle-Kreis et al., 2007). Particles formed by condensation in the diluting exhaust plume are generally in the size range below 30 nm and are formed as the hot exhaust gases are expelled from the tailpipe of a vehicle, creating large numbers of very small particles in the air.

5 They are semi-volatile and consist mainly of hydrocarbons and hydrated sulphuric acid (Shi et al., 2000; Caravaggio et al., 2007). The conditions influencing the production of these semi-volatile nanoparticles and hence the shape of the particle size distributions, include dilution rate, dilution ratio and temperature.

As dilution increases downwind from the roadway, the concentration of organic vapours decreases, enhancing evaporation of the semi-volatile species from particle surfaces to re-establish equilibrium (Zhang et al., 2004). Volatility may explain the more rapid decay in particle concentration compared to the concentrations of non-labile PM species (such as elemental carbon) or gaseous pollutants (such as CO and NO<sub>x</sub>) with increasing distance downwind from the roadway. However, Zhu et al. (2002) attributed the decreased particle number concentrations, and change in particle size distribution with increasing distance from the freeway, to both atmospheric deposition and coagulation. In the “road-to-ambient” process, dilution and condensation are dominant. Coagulation is slow compared to the dilution timescale and hence unlikely to be important (Zhang and Wexler, 2004). Jacobson et al. (2005) accepted the model proposed by Zhang et al. (2004), in which coagulation was not considered an important factor, and only condensation/evaporation and dilution were considered. Jacobson et al. (2005) proposed a new explanation suggesting that small liquid nano-particles shed semi-volatile organics almost immediately upon emission. The shrinking of these nano-particles due to evaporation enhances coagulation of these smaller particles by over an order of magnitude. Lipsky and Robinson (2006) reported the effects of dilution on fine particle mass and the partitioning of semi-volatile organics in diesel exhausts. A large decrease in fine particle mass was observed with increased dilution. Emissions of elemental carbon did not vary with dilution, and the changes in fine particle mass were caused by changes in the partitioning of semi-volatile compounds. Birmili

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et al. (2010) have demonstrated the semi-volatility of traffic particles of <60 nm using a thermodenuder system. According to Ntziachristos et al. (2007), particle size distributions next to a diesel freeway showed a bimodal distribution, with a nucleation mode below 40–50 nm and an accumulation mode peaking at 70–80 nm during all sampling hours. Currently, the uncertainties in relation to vehicle emission factors for ultrafine particles from motor vehicles are still considerable – both for particle sizes ranges and for particle numbers. Particle formation in diluting engine exhaust depends strongly on meteorological factors (Charron and Harrison, 2003), and therefore an understanding of the evolution of nanoparticles in urban environments must include all the factors described. Nonetheless, emission factors determined in dynamometer studies have been found to well reflect those estimated from roadside measurements (Beddows and Harrison, 2008).

Many studies have focused on the evolution of vehicular particles during advection away from the source; very few studies have focused on the vertical variations of particle number concentrations and size distributions. Li et al. (2007) reported that coagulation and dilution processes were the only factors causing changes to particle size distributions at vertical levels. In their data, size distributions differed between May and November. A finer mode was evident during the warmer month, but not seen in November. The different modes were attributed to nucleation processes of the semi-volatile matter emitted from vehicles. Kerminen et al. (2007) reported much smaller particle concentration dilution factors (1.1–1.3) with low wind speeds coupled with temperature inversions. Under such conditions, processes such as condensation, evaporation and coagulation are inefficient. Evaporation was given as a possible contributing cause for the decrease in 7–30 nm particle number concentrations for the sites more distant from the road. Other studies have determined the concentrations and size distributions of fine particles measured at roof level in an urban zone, showing an increase in particle concentration over the whole size range measured, but detected one hour later than the traffic peak at street level (Despiau and Croci, 2007). Particle number concentrations measured at street level were about 6.5 times higher than at rooftop. Conversely,

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rooftop particle number concentrations in the 5–30 nm size range increased with wind speed, whereas those for particles between 30 and 300 nm did not vary with wind speed (Kumar et al., 2009). To our knowledge, there are no studies where remotely sensed profiles of urban turbulence were taken simultaneously with aerosol size distributions measured at different altitudes. Janhäll et al. (2006) reported Lidar data used to follow the break-up of the overnight inversion, but did not link that directly with particle size distributions measured at different heights.

The objective of the present paper is to report spatial variations in particles emitted from traffic and to observe the evolution of size distributions with distance and time by taking measurements simultaneously at three sites within the urban area of London. The aerosol measurements were also coupled with Doppler Lidar remote sensing measurements in order to study the effect of boundary layer dynamics upon the aerosol populations, by considering measurements of both mixing heights and atmospheric turbulence.

## 2 Methods and data analysis

### 2.1 Sampling sites

REPARTEE (Regents Park and Tower Environmental Experiment) was a multi-site study of aerosols and gases in the atmosphere of London (UK). More information can be found in Harrison et al. (2010). During the REPARTEE field campaigns held for four weeks each in both October 2006 and October/November 2007, measurements of particle number concentrations were made using condensation particle counters, and number size distributions using Scanning Mobility Particle Sizers deployed at locations in central London.

Sampling took place in 4 different locations (see Fig. 1):

- *Marylebone Road (MR)*. This site is located on the kerbside of a major arterial route within the city of Westminster in London. The surrounding buildings form

a street canyon. Traffic flows of over 70 000 vehicles per day pass the site on 6 lanes with frequent congestion. This site is classified as a roadside site. The sample inlet is at a height of about 3 m.

- *BT Tower (BT Tower)*. This is the operational tower of British Telecom (60 Cleveland Street); the cylindrical tower stands 189 m above the ground. Measurements were taken from the 35th floor at about 160 m above ground level on a well ventilated balcony. The site is about 350 m south of Marylebone Road and 1.1 km east of the Marylebone Road measurement site.
- *Inner Circle of Regents Park (R. Park)*. This is a major park within the city of London extending to 166 hectares (410 acres). The air sampling inlet was at 10 m. The site is located away from local roads and is about 600 m north of Marylebone Road, which is the nearest major highway.
- *North Kensington (NK)*. This is sited in the grounds of Sion Manning School in St Charles Square, North Kensington, surrounded by a mainly residential area. The height of the inlet is approximately 3 m. The site is classified as Urban Background by the UK automatic air quality network and is situated about 4 km east of the 3 sites described above. The pollution climate at this site has been analysed in detail by Bigi and Harrison (2010).

## 2.2 Particle number concentrations

Three of the sites (MR, BT Tower and NK) used the same type of particle counter (TSI Model 3022A; lower 50% cut-point 7 nm) whilst the instrument in R. Park was a TSI 3776 (with a lower 50% cut-point at 2.5 nm) which would lead to slightly higher readings on the latter instrument. The CPC data used in this paper were collected during the REPARTEE II field study (17/10/2007:09/11/2007; 24 days in total).

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## 2.3 Aerosol size distributions measurements

The size distribution data presented derive from the two REPARTEE campaigns, supplemented by additional data as outlined below. A combination of measurements from different years is used to investigate particle dynamics for sizes between 3 nm and 500 nm. This is supplemented by a study of particles in the size range 20 to 500 nm from three measurement sites simultaneously. The former study allows the ultrafine mode to be characterised, the latter demonstrates that the different studies are comparable despite being undertaken at different times.

### 2.3.1 Non-simultaneous SMPS and nano-SMPS measurements

- Data from MR were taken in October 2003 with a nano Scanning Mobility Particle Sizer (SMPS) system comprising a Model 3080N nanoclassifier and a Model 3025 Ultrafine Condensation Particle Counter (UCPC). This allowed the measurement of particles in the range 5–184 nm (Charron and Harrison, 2005).
- Data from the BT Tower were collected using two SMPS systems in October 2007 (REPARTEE-II). The first comprised a Model 3080 Electrostatic Classifier and a model 3022A Condensation Particle Counter (CPC). The classifier was configured to allow particles in the range 14.9–673.2 nm diameter to be counted and the sample time was 4 min 30 s (scan 120 s + retrace 15 s × 2 scans per sample). The second system comprised an EC model TSI 3085 and CPC model TSI 3025 allowing counting in the particle size range 4.53–159.6 nm. Sample time was 4 min 30 s (scan 120 s + retrace 15 s × 2 scans per sample).
- Size distribution measurements at Regents Park were made using a Differential Mobility Particle Sizer (DMPS), covering the size range of about 3 to 830 nm diameter, during the month of October 2006 (REPARTEE-I). The DMPS consists of two “Vienna” style Differential Mobility Analysers (DMAs), as described by Williams et al. (2007), an ultrafine DMA (effective length 11 cm) for particles in the size range

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3.4–34 nm and a standard DMA (effective length 28 cm) for particle sizes from 30–830 nm. The aerosol particles were then counted using condensation particle counters (CPC). The ultrafine DMA was attached to a TSI 3025 ultrafine CPC (particle detection limit 50% at 3 nm) and the standard DMA, to a TSI 3010 CPC (particle detection limit 50% at 10 nm).

In summary, nano-SMPS data were available for the 3 different sites (MR, R. Park and BT Tower) for the same month of the year (October) but the measurements were taken in different field studies for each site (2003, 2006 and 2007 for MR, R. Park and BT Tower, respectively). The year to year variation in the particle size distributions collected at Marylebone Road over the year 2000, 2001 and 2003 was found to be minimal (Charron and Harrison, 2003, 2005), allowing a comparison of particle size distributions taken at the same point during the same period (autumn) but in different years.

## 2.4 Simultaneously deployed SMPS systems during REPARTEE II

During REPARTEE II three SMPS systems were deployed simultaneously in the three different locations (road, background and tower sites), providing real time measurements of the particle size distributions at the 3 different sites. Two identical systems were used at the tower and at the park (both classifier TSI 3080 and CPC 3022A), whilst the SMPS at the Marylebone road site used the same TSI 3080 EC but with a different CPC – model TSI 3776. The SMPS at the park and at the tower were sited together and inter-compared over a two-day period; they were found to agree very closely with each other, and to the SMPS at the MR site. Particle losses were calculated and used to correct the measured data. A summary of the different datasets explained in Sects. 2.3.1 and 2.3.2 is presented in Table 1.

## 2.5 Organic carbon (OC) and elemental carbon (EC) measurements

Continuous collection of 24 h, midnight to midnight GMT  $PM_{2.5}$  and  $PM_{2.5-10}$  particles was carried out using two dichotomous Partisol-Plus Model 2025 Sequential Air Samplers, fitted with  $PM_{10}$  inlets. The instrument contains a virtual impactor and downstream flow controllers which separate the flow into fine and coarse fractions, at flow rates of  $15.0\text{ L min}^{-1}$  and  $1.7\text{ L min}^{-1}$ , respectively, from which particles were collected on quartz fibre filters (QM/A). The coarse particle sample was corrected for the collection of fine particles from the carrier flow. Sampling took place at R. Park and BT Tower from 2 October 2006 to 30 October 2006. Data capture was about 80% for simultaneous measurements at both sites. Elemental and organic carbon data were obtained by a Sunset Laboratory Thermal-Optical Carbon Aerosol Analyzer which uses thermal desorption in combination with optical transmission of laser light through the sample to speciate carbon (Sunset Laboratory Manual, 2000) using the protocol described by Harrison and Yin (2008). Organic carbon is removed during an initial non-oxidizing temperature ramp from ambient to  $700^\circ\text{C}$  under a helium atmosphere, and then passes to a manganese dioxide oxidizing oven where it is converted to carbon dioxide, which is mixed with hydrogen and converted to methane over a heated nickel catalyst. The methane is subsequently measured using a flame ionization detector (FID). A second temperature ramp from  $550^\circ\text{C}$  to  $850^\circ\text{C}$  is then initialized with the carrier gas switched to a helium/oxygen mixture, under which elemental carbon and pyrolysis products are oxidized and carried through the system and measured in the same manner as the organic carbon. A laser is used to monitor the light transmission through the filter during the analysis, which determines a split point that separates the elemental carbon formed by charring during the initial non-oxidizing temperature ramp from the elemental carbon that was originally in the sample. The split point is the point in time when the laser signal measured during the oxidizing stage equals the initial laser signal. Both external (sucrose solution) and internal (methane gas) carbon standards are used for FID calibration.

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## 2.6 SMPS clustering analysis

The 3 SMPS systems deployed simultaneously during REPARTEE-II (17-10-07 to 09-11-07) generated approximately 7,000 SMPS size distributions at 5 minute resolution at each site. These size distributions were averaged over 1 hour periods reducing their number from about 20 000 to 1567, which were subsequently normalised by their vector-length and cluster analysed (Beddows et al., 2009). The same size distributions were averaged also over 6 h intervals (00–06, 06–12, 12–18, 18–00) reducing their number to 259 and these results are presented elsewhere (Beddows et al., 2009). The cluster analysis differentiated the spectra into a small number of size distributions based upon similarities in their size distributions. The objective of this paper required a higher time resolution (1 h) in order to see the evolution of UF particles in the atmosphere. The Dunn-Index for the results of the K-means analysis for different cluster numbers showed a clear maximum for 22 clusters, some of which belonged only to specific sampling sites and to specific times of the day. One advantage of this clustering method over providing an average of aerosol size distributions is that it does provide a specific number of size distributions which can be compared across different time periods (Beddows et al., 2009). The intensive observations of aerosol size distributions were used with trace gas data and measurements of boundary layer dynamics to quantify the variability in urban aerosols caused by both chemical and meteorological processes.

## 2.7 Doppler Lidar description and height estimation methods

The Doppler Lidar permits the detection of the boundary layer (BL) top, mixing height and aerosol layer top with a vertical resolution within a few tens of metres and a temporal resolution in the range of seconds to minutes. Further Lidar results and analysis from the REPARTEE II campaign are more fully described in Barlow et al. (2010). The instrument was a Halo Photonics 1.5  $\mu\text{m}$  scanning Doppler Lidar (provided by the UK Facility for Ground-based Atmospheric Measurements (FGAM)) and operated by the

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University of Salford; a full description of the instrument is given in Pearson et al., (2009). It was installed in the car park of the University of Westminster on the Marylebone Road directly adjacent to the air sampling station and was running continuously for three weeks between 24 October and 14 November 2007. Due to the proximity and height of the neighbouring buildings, the Lidar was restricted to making only vertical stare measurements, i.e. directly upwards. During this study the Lidar was set to have a vertical resolution of 30 m and was focussed at 2 km in order to maximise the signal from the boundary layer. This resulted in a total of 66 measurement range gates (i.e. height layers). The Lidar returns a measurement of backscatter and a Doppler velocity measurement every 4 s, from which turbulent statistics in the boundary layer can be calculated. The vertical velocity variance is used to calculate the mixing height,  $z_{MH}$ , i.e. the height to which aerosols are expected to be mixed from the surface vertically due to turbulent transport (Siebert, 2000). From the Lidar measurements, the mixing height was defined as the height in the boundary layer up to which a threshold of  $\sigma_w^2 > 0.1 \text{ m}^2 \text{ s}^{-2}$  is met ( $\sigma_w^2$  is the variance of the vertical wind velocity). This threshold was determined by examining the sensitivity of derived mixing heights to the chosen threshold value until a reasonable (i.e. physically realistic) range of mixing heights was obtained. It is recognized that this choice is somewhat arbitrary, as explored in some detail by Barlow et al. (2010). A second height is determined through examination of the gradient in the backscatter profile. At the boundary between two layers of differing aerosol concentration, there will be a sharp change in the gradient of the backscatter. The lowest, ground-based aerosol layer can be detected by finding the first significant negative gradient in the backscatter looking from the surface upwards. A significant negative gradient in the backscatter was defined quantitatively as less than  $-0.03$  (arbitrary units). Again, this criterion was found by examining the sensitivity of the derived aerosol layer depth until a satisfactory range of heights were found. Herein, this height is referred to as  $z_{AER}$ . Further details of the methods for detecting different layer heights are given in Barlow et al. (2010).

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## 2.8 Gas measurements and meteorological data

Measurements of trace gases (NO, NO<sub>2</sub> and O<sub>3</sub>) and meteorological variables (relative humidity, RH and temperature, *T*) used for the ground site were taken from the North Kensington (NK) site (data taken from the UK Air Quality Archive: [www.airquality.co.uk](http://www.airquality.co.uk)).

5 In each case O<sub>3</sub> was measured by UV absorption, NO by chemiluminescence and NO<sub>2</sub> by thermal conversion (heated Mo catalyst) / chemiluminescence; the NO<sub>2</sub> signal may therefore be subject to interferences from other NO<sub>y</sub> compounds (Dunlea et al., 2007). Meteorological variables were also measured at the BT Tower using a Vaisala WXT510 weather station located on top of the tower at 190 m. In both cases, measurements  
10 were continuous throughout the campaigns.

## 3 Results

### 3.1 Nano particle evolution

Figure 2 shows the average diurnal pattern of particle number concentrations at all four sites. This shows a clear gradient in number concentrations from Marylebone Road, peaking at around  $100 \times 10^3 \text{ cm}^{-3}$ , to Regents Park (around  $38 \times 10^3 \text{ cm}^{-3}$ ), to North Kensington ( $25 \times 10^3 \text{ cm}^{-3}$ ) and the BT Tower ( $9 \times 10^3 \text{ cm}^{-3}$ ). The high ratio in particle  
15 number concentrations between the ground-based sites and the BT Tower is unlikely to be explained by dispersion processes alone. The average ratio for all hours throughout the entire campaign for particle number concentration between the BT Tower and North Kensington, (which used identical samplers) was  $0.39 \pm 0.12$  (s.d.) whereas the  
20 ratio of elemental carbon in PM<sub>10</sub> particles between the BT Tower and R. Park averaged  $0.57 \pm 0.10$  (Table 2) – obtained from 24-h Partisol samples. A regression of the EC concentrations at the BT Tower and R. Park sites showed a relationship of BT Tower =  $0.66 \text{ R. Park} - 0.27 \mu\text{g m}^{-3}$  ( $R^2 = 0.92$ ). Recent work (Harrison and Yin, 2008)  
25 has shown that elemental carbon is an excellent tracer of diesel exhaust emissions

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and it is a species with a relatively long atmospheric lifetime which is a useful tracer of ground-level urban emissions. The data demonstrate a major loss of particle number on the Tower relative to ground-level measurements in the footprint region, taking account of elemental carbon as passive tracer.

Further evidence on this phenomenon comes from a comparison of particle size distributions at the three sites (Fig. 3), constructed from data collected as outlined in Sect. 2.3. A second independent study, in which three identical SMPS systems were deployed concurrently at the three locations (DMA TSI 3080 and CPC TSI 3022A, size range 15.1–661 nm) with matched inlet systems over the same time period (October 2007) shows the same trend reported in Fig. 3 (see Sect. 3.2), but does not extend to the smaller particle sizes. More details on this independent study are given in the next section.

The size distribution measured at Marylebone Road is typical of roadside and on-road number size distributions, peaking between 20 and 30 nm diameter (Charron and Harrison, 2003; Ronkko et al., 2007). In contrast, data from the Regents Park site show a mode which has shifted downwards to below 10 nm diameter together with some overall loss of area under the curve, representing a loss of total particle number. In contrast, the data from the BT Tower show a minor mode at around 20 nm, whilst the major mode is in the region of 100 nm diameter typical of the involatile graphitic particles in engine exhaust, and accumulation mode particles from other sources. This mode is also visible as a shoulder in the other size distributions. When a curve-fitting programme is used to disaggregate these size distributions into a number of log-normal distributions and the Marylebone Road data are compared with Regents Park (Fig. 4), both datasets show the mode at 40–60 nm and a mode at around 15–20 nm, which is much reduced in the Regents Park data. At Regents Park but not Marylebone Road, a further mode peaking at around 6 nm was observed. We believe this arises from the evaporation of particles initially in the 20 nm diameter mode during advection into the Park, and is consistent with the involatile particle core measurements for diesel exhaust reported by Ronkko et al. (2007) and Kirchner et al. (2009). Average data from

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the BT Tower show modes at around 100 nm (non-volatile traffic particles and long-range transported secondary components), and 25 nm, which we interpret as traffic particles which are seen only during daytime (Fig. 5). The sub-10 nm mode at Regents Park could conceivably arise from localised nucleation processes, but the diurnal pattern gave no strong support to this concept, and fluctuations in particle concentrations correlated with NO<sub>x</sub> and black carbon, indicating a traffic source.

### 3.2 Simultaneous SMPS measurements during REPARTEE II

Figures 3 and 4 were obtained with aerosol size distribution measurements taken in London during the same month of different years (October 2003, October 2006 and October 2007). During REPARTEE II, three SMPS systems were deployed simultaneously at 3 sites in London providing aerosol size distributions in the range between 15 nm and 550 nm. The data shown in Figs. 5 and 6 demonstrate how the exclusion of particles below 15 nm in diameter results in an incomplete description of the nanoparticle evolution towards smaller sizes, simply because the mode below 10 nm seen at R. Park is totally missed. Nevertheless, the 3 SMPS systems deployed simultaneously in London during REPARTEE II help to support the conclusions derived from Fig. 3 as they provide measurements taken simultaneously, hence overcoming the weakness that the previous dataset combines measurements from different campaigns. Figure 5 shows the average size distributions from REPARTEE II at the MR, R. Park and BT Tower sites for the 6 h time periods at 00:00–06:00 (A), 06:00–12:00 (B), 12:00–18:00 (C) and 18:00–24:00 (D), respectively. As expected, the road site presents the highest aerosol particle number concentration, with the modes at about 20–30 nm and 60–80 nm as already described in Fig. 3 and elsewhere (Charron and Harrison, 2003). The aerosol size distributions at the R. Park site for the warm part of the day (Fig. 5c) show a shift of the mode at 20 nm towards smaller sizes, confirming the finding of Fig. 3. The average size distributions from the BT Tower site do not change dramatically, other than for a higher number of particles below 50 nm during daytime (Fig. 5b and c). Whilst Fig. 5 is important to indicate the variability across the

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three different sites for the same simultaneous sampling time, Fig. 6 shows the variability of the aerosol size distributions at the same site but for different parts of the day (6 h intervals). Figure 6a shows the higher particle number concentrations for rush hour periods (green and black lines) detected at the MR site. Figure 6b, representing Regents Park, shows the overall lowest aerosol particle number loading for the nighttime (red line). The rush hour time intervals (green and black) are characterised by a higher number of particles below 50 nm reflecting the traffic emissions detected also at the R. Park site. Interestingly, during the warmest part of the day (blue line, 12:00–18:00) the smaller mode at about 20–30 nm is observed to reduce from about 27 nm to 18 nm. Although limited to the interval 15–650 nm, these findings support those described in Figs. 3 and 4 where nano-SMPS systems were used and shows a shift of particles towards smaller sizes presumably due to evaporative loss of material as it is advected from the traffic source.

Figure 6c shows the average size distributions for the 4 different time periods at the BT Tower site. A higher particle number concentration for particles smaller than 25 nm can clearly be seen for daytime periods (06:00–18:00, blue and green lines) in comparison to the nighttime periods (18:00–06:00, red and black lines). This clearly reflects the fact that small particles emitted within London are transported vertically to the height of the tower more efficiently during the day than at night when mixing is suppressed and the surface layer may not extend to the measurement height on the Tower (e.g. Barlow et al., 2010). Martin et al. (2009) measured total particle number flux at the BT Tower during REPARTEE I and found strong diurnal cycles with pronounced weekend versus weekday differences which can be linked to traffic activity. The present study not only reports total particle number concentrations but also provides unique aerosol size distribution data illustrative of the dynamics of the aerosol populations across different sites. An in-depth analysis of the evolution of the size distributions of particles detected at the BT Tower site, coupled with Dopplar Lidar measurements is given in the next section.

### 3.3 The effect of boundary layer dynamics on the aerosol size distributions over London

The Lidar measurements give high-resolution information about the structure of the boundary layer and the turbulence and aerosols present within it. Two different heights are defined in Barlow et al. (2010): the Boundary Layer top, where there are large gradients in properties between the free atmosphere which is relatively aerosol free compared with the polluted BL below; and a lower aerosol layer depth connected to the ground, ( $z_{\text{AER}}$ ). This is a layer of aerosol adjacent to the surface, more common at night when the depth of mixing was limited. Turbulence statistics derived from the Lidar were also used to determine mixing heights. The mean variance of the vertical wind velocity ( $\sigma_w^2$ ) between 100–250 m was calculated over half hour periods and is taken as a surrogate for the turbulence strength. For this study, the urban BL heights and the  $\sigma_w^2$  values were averaged to one hour resolution. The size distribution data were disaggregated according to whether  $z_{\text{MH}}$  was below or above the height of sampling on the tower (160 m). Hence all Lidar gates of 150 m and below were combined into the former category and those of 180 m above into the latter. Data from the 150–180 m Lidar gates were not used. Figure 7 shows the average nano-SMPS size distributions (5–140 nm) collected during REPARTEE II at the BT Tower site for different values of two variables obtained from the Lidar.

The data in Fig. 7 were disaggregated as follows: average nano-SMPS size distributions for BL above 180 m (BL>180 m, red line) and BL below 150 metres (BL<150 m, black line) for all the Lidar datapoints. Furthermore, the data for BL>180 m were divided into periods of high turbulence ( $\sigma_w^2 > 0.5 \text{ m}^2 \text{ s}^{-2}$ ; green line) and low turbulence ( $\sigma_w^2 < 0.5 \text{ m}^2 \text{ s}^{-2}$ ; blue line). When comparing size distributions for the BL above and below the BT Tower sampler, there is an enhancement of particles smaller than 50 nm for the former case. This is even more evident when considering periods of high turbulence relative to the periods of lower turbulence (blue and green lines, respectively).

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Under conditions when the tower sampler was above the mixing height, the greatest abundance of accumulation mode particles accompanied the lowest abundance of sub-50 nm particles. A deep boundary layer and high turbulence is associated with the lowest abundance of accumulation mode particles and the highest numbers of sub-50 nm particles. The  $\text{NO}_x$  data (Table 3) also show slightly higher mean concentrations at the tower site with a shallow boundary layer (<150 m) than when boundary layer is deeper (>180 m). The fact that enhanced mixing leads both to an increase in sub-50 nm particles and a decrease in the larger-sized accumulation mode peak is at first sight surprising. However, the Lidar backscatter data (Barlow et al., 2010) shows a decrease in light scattering aerosol (close in size to 1.5  $\mu\text{m}$ , the wavelength of the Lidar) with height above the top of the mixing height. Hence enhanced mixing associated with a deepening boundary layer not only carries polluted air from below (with much enhanced sub-50 nm particle concentrations, but comparable accumulation mode levels), but also cleaner air from above leading to the reduction in accumulation mode concentrations. This interpretation is supported by the  $\text{NO}_x$  data in Table 3 which show a decrease as the mixing height extends above the height of the sampler. It cannot be ruled out that of nucleation processes taking place aloft contribute to the enhancement of sub-20 nm particles at the Tower, and similar processes have been suggested by Wehner et al. (2010). Kumar et al. (2009) attributed the production of nucleation mode particles (and also a nucleation event) at rooftop level to both the production of new particles through gas-to-particle conversion and photochemically induced nucleation, since conditions were found to be favourable for both processes. Our data give no obvious indication of new particle formation from nucleation processes, but our earlier work in a UK city has shown this to be a relatively infrequent occurrence at ground-level (Alam et al., 2003). The fact that air at the sampling height on the Tower retains high concentrations of  $\text{NO}_x$  and accumulation mode particles but is heavily depleted in sub-50 nm particles when isolated from the source below, is a clear indication that the lifetime of surface-derived sub-50 nm particles is short compared to that of  $\text{NO}_x$  and larger particles.

Complementary physical and chemical data for the periods used for generating Fig. 7 can also be seen in Table 3, where gas measurements and basic meteorological parameters are given for the 4 different scenarios. More information on other parameters, including wind speed, can be found in Barlow et al. (2010). The difference in temperature values between the ground site and the tower site are larger during periods with high  $\sigma_w^2$  and deep boundary layer. This is expected, as the temperature gradient between the ground level and the air creates much of the turbulence through convection.

Concentrations of ozone were normally higher at the tower in comparison to the ground sites; in contrast higher values of  $\text{NO}_x$  were found at the ground sites. Again, this is expected as nitrogen oxides are emitted by traffic and the high ground-level NO serves to reduce the ozone. For similar values of  $z_{\text{MH}}$ , a greater dispersion of  $\text{NO}_x$  (lower concentrations) can be seen at the North Kensington background site with higher turbulence levels. For high turbulence values the differences between the tower and the ground sites were found to be much reduced (in comparison to low turbulence values) reflecting more efficient mixing.

Further evidence for the evaporation and the dispersion of traffic related particles is derived by comparing the Lidar measurements with the SMPS data clustered according the method described by Beddows et al. (2009). Data from around 7000 SMPS size distributions were pooled from all three sites from the REPARTEE II campaign. Eleven of the 22 SMPS size distribution clusters obtained were found to occur mainly at the BT Tower site, the others were associated with size distributions collected at the MR and R. Park sites. By comparing clusters of specific size distributions with the hourly averaged  $\sigma_w^2$  (taken at the Lidar height interval 100–250 m, i.e. around the sampling height on the tower), we can associate an average value of turbulence to a specific SMPS size distribution obtained by clustering the measurements taken at the BT Tower. Figure 8 shows the 11 SMPS clusters describing the SMPS size distributions sampled at the BT Tower site. Two main modes can be seen: the first at about 80–120 nm representing the accumulation mode and a second, peaking at about 20–30 nm. The two most distinct clusters are cluster 14 and cluster 6, with enhanced modes at 80–120 nm and

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20–30 nm, respectively. The smaller mode can also be seen in Fig. 3, and is attributed to (un-evaporated) traffic related particles seen at the Tower only during daytime. Clusters 11 and 10 contain instead about the same abundance of both aerosol size modes. The legend of Fig. 8 also reports the average values for  $\sigma_w^2$  for each of the 11 SMPS clusters. The clusters with the most pronounced mode at 20–30 nm are the ones associated with the higher turbulence (i.e. cluster 6 for example presents an average  $\sigma_w^2$  of  $1.26 \text{ m}^2 \text{ s}^{-2}$ ). By taking the total number of particles below 30 nm of each SMPS cluster and regressing it upon the average values of turbulence, an  $R^2$  value of 0.86 was calculated (Fig. 8). To our knowledge, these are the first results published in the literature showing a clear linkage between turbulence values obtained by Lidar and simultaneous SMPS measurements taken above a city. Figure 8 also shows that cluster 6 and cluster 7 (with the highest values of average  $\sigma_w^2$  of 1.26 and  $0.93 \text{ m}^2 \text{ s}^{-2}$ , respectively) exhibit the smaller mode shifted towards the smallest detectable sizes below 19 nm. In contrast, clusters characterized by a lower  $\sigma_w^2$  (cluster 1 and cluster 11, for example with  $\sigma_w^2$  of 0.78 and  $0.51 \text{ m}^2 \text{ s}^{-2}$ , respectively) show a nucleation mode above 25 nm.

## 4 Implications and conclusions

The main primary pollution source of  $\text{NO}_x$  and particulate matter in central London is road traffic, with space heating also a source of emissions. Regional transport is a major source of secondary particulate matter. This work treats the source signature of Marylebone Road as representing the fresh nanoparticle source in London's air. According to the UK Air Quality Expert Group (AQEG, 2005), road traffic accounted for almost 50% of ultrafine particles ( $\text{PM}_{0.1}$ ) emissions in the UK in 2001. Other high temperature sources, notably industries such as electricity generation and iron and steel contribute, but are much less important (AQEG, 2005) and more significantly, they are not sited in London (with minor exceptions). Shi et al. (2001), working in Birmingham (UK), detected nanoparticle plumes from large combustion sources, but concluded that by far the major contributor was road traffic. The other source which needs to be

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considered is widespread photo-chemically induced nucleation of particles (Kulmala et al., 2007) which occurs quite frequently at rural sites in the UK (Charron et al., 2007). Alam et al. (2003) made detailed measurements in Birmingham (UK), observing that out of a total of 232 days sampling distributed throughout the year, nucleation events occurred on only eight days which could be attributed fairly unequivocally to homogeneous nucleation processes, with a further four days possibly attributable. The primary reason is the large condensation sink on existing aerosol available in the UK urban atmosphere, a feature of London to an even greater degree than of Birmingham (UK). Consequently, we are confident in attributing the observed sub-50 nm particle fraction predominantly to traffic emissions.

Charron and Harrison (2003) have previously demonstrated that the particle number concentration in roadside air is strongly influenced by the dilution conditions in ways that can be explained by the formation of particles in the mode centred on 20–30 nm by condensation processes in the diluting engine exhaust. This strongly suggests that such particles are semi-volatile and the only previous evidence of their loss by evaporation in the atmosphere (Zhang et al., 2004), as opposed to artificial heating (Kuhn et al., 2005; Biswas et al., 2007) comes from studies downwind of a Californian freeway. Our own group (Shi et al., 1999) and Fushimi and co-workers (Fushimi et al., 2008) have shown a shift in the modal diameter of >10 nm particles to larger sizes on moving away from the roadside, but both sets of observations could plausibly be explained by dilution of traffic particles to larger sizes by a coarser background aerosol. This study suggests that even within the urban atmosphere, on distance scales of the order of 1 km and travel times of around 5 min upon moving away from major emissions sources, a very significant loss of the nanoparticle fraction is observed which manifests itself in a shift to smaller sizes within Regents Park and an almost complete loss of the sub-30 nm mode at the BT Tower site. The size distribution here is very similar to that observed at the rural Harwell site in the absence of new particle formation or local emissions (Harrison, 2007). Given that total number concentrations are  $\sim 10^4 \text{ cm}^{-3}$ , coagulation will be far too slow to explain significant reduction in particle numbers. As the semi-volatile

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particles form by condensation onto an involatile core (Ronkko et al., 2007; Sakurai et al., 2003) (typically of sulphuric acid or solid nuclei originating from the engine), it is likely that the cores of particles remain but are too small to be observed with high efficiency with particle counters such as the TSI 3022A. According to Ronkko et al. (2007), the involatile core is about 5 nm diameter and to Kirchner et al. (2009) 1–3 nm, whilst the efficiency of the 3022A is only 50% at 7 nm, and less below this size. Such particles would be subject to very rapid dry deposition processes. The absence of such a mode in the BT Tower data suggests that the involatile core in the London traffic aerosol may be smaller than 5 nm. Gramotnev and Ristovski (2004) also reported a complex evolution of small aerosol traffic modes shifted towards smaller particle size. Our study is much more comprehensive as it considers a number of sites (4) within the London urban area and a very large set of data taken both simultaneously and across different years. Davison et al. (2009) measured inexplicable increasing gradients in particle number concentration with distance from a highway, but the particle numbers were so low that the traffic particles may not have been sampled.

Some of the attempts to model the behaviour of traffic-generated nanoparticles in the urban atmosphere have totally failed to account for their semi-volatility (Gidhagen et al., 2005; Clarke et al., 2004). In comparison, adjustment of the size distribution through coagulation is very slow. Our results demonstrate that any effective model needs to take account of these processes and that particle exposure, both in terms of number concentration and size distribution, is likely to be highly sensitive to the location of sample collection. In a recent paper, Robinson et al. (2007) provide compelling evidence for the partial evaporation of organic particulate emissions with subsequent slow conversion of the volatile fraction to secondary organic aerosol. Our results are highly consistent with the former of these processes affecting particles in London.

The data here presented give fascinating insights into the dynamics of particle size distributions in urban air. The times involved in the advection of air polluted by traffic emissions into the centre of R. Park are of the order of 10 minutes for wind speeds of 2–5 m per second and travel distances of 1–2 km from major source areas. Vertical



dispersion of ground-level emissions to the top of the tower takes around 5 min in conditions of high turbulence, and 10 min in more stable conditions (Barlow et al., 2010). Hence on timescales of a few minutes, substantial evaporative shrinkage (and apparent loss, depending on the measurement device) of traffic-generated nanoparticles is occurring, with potentially far-reaching implications.

In particular, the implications of these results for human health are profound. If the particles which are “lost” have an involatile core, the total number concentration is not immediately changed by the evaporation phenomenon as the particles have simply become too small to be observed by the conventional condensation particle counters. However, the very substantially smaller particles are subject to more rapid loss by coagulation and dry deposition processes. Perhaps more importantly, by virtue of their very high diffusivity, they are unlikely to penetrate the human respiratory system as far as the alveoli, depositing preferentially in the upper airways (ICRP, 1993). In contrast, the peak in the alveolar regional deposition efficiency of particles is around 30 nm, corresponding approximately to the mode in the size distribution in roadside air. However, whatever the true fate of the “lost” particles, it would appear that the threat to human health is reduced by a far greater factor than would be afforded by dispersion and dilution processes alone. This may be a contributory factor in the recent observations that reductions in FEV<sub>1</sub>, and FVC in asthmatic subjects were significantly larger when exposed to ambient air in Oxford Street, London, as opposed to nearby Hyde Park (McCreanor et al., 2007).

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**Table 1.** Summary of SMPS data availability for different years. X represents data available and used in this study.

Year	M. ROAD		R. PARK		BT TOWER	
	Nano	Normal	Nano	Normal	Nano	Normal
2003	X					
2006 (REPARTEE-I)			X	X		
2007 (REPARTEE-II)		X		X	X	X



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**Table 2.** Ratio of particle number count from CPC to organic carbon and elemental carbon concentrations for three sites.

<i>Site</i>	<i>CPC model</i>	<i>CPC counts/ PM<sub>2.5</sub>OC mass</i>	<i>CPC counts/ PM<sub>2.5</sub>EC mass</i>
BT Tower	3022	4145 ± 1872	11425±3877
North Kensington	3022	7683 ± 2074	14699 ± 3280
R. Park	3776	10049 ± 3351	19005 ± 6745

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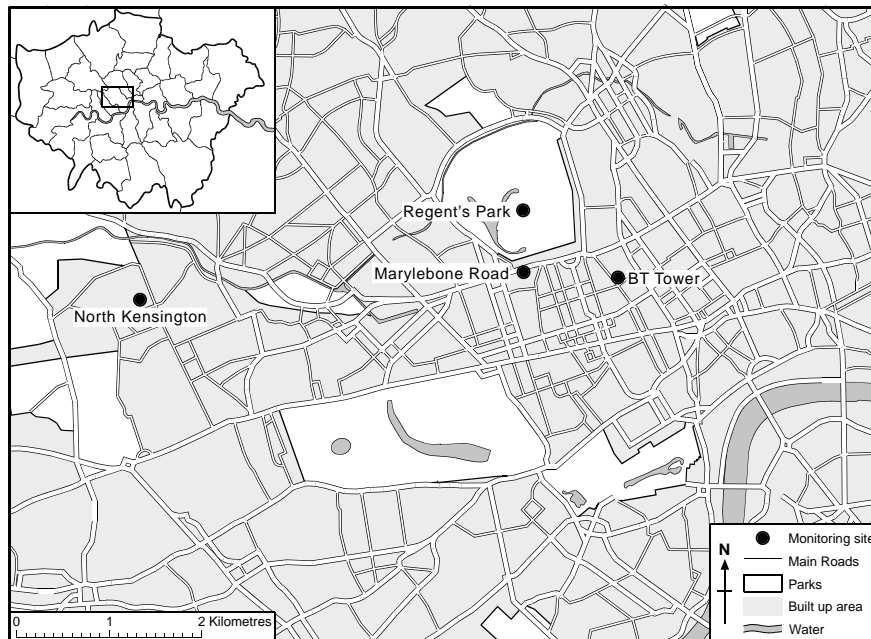
**Table 3.** Concentrations (mean  $\pm$  s.d.; ppb) of  $\text{NO}_x$  and  $\text{O}_3$  at ground level (NK) and aloft on the Tower (BT Tower) as a function of mixed layer depth (BL) and turbulence level (low is  $\sigma_w^2 < 0.5 \text{ m}^2 \text{ s}^{-2}$ ; high is  $\sigma_w^2 > 0.5 \text{ m}^2 \text{ s}^{-2}$ ). Units are in ppb for gas measurements, degrees Celsius for temperature ( $T$ ) and % for Relative Humidity (RH).

	$\text{NO}_x$		$\text{O}_3$		$T$		RH	
	Ground	Tower	Ground	Tower	Ground	Tower	Ground	Tower
BL < 150 m	81 $\pm 75$	22 $\pm 16$	4 $\pm 7$	16 $\pm 7$	9.4 $\pm 2.4$	7.8 $\pm 1.8$	84 $\pm 12$	80 $\pm 10$
BL > 180 m	35 $\pm 26$	21 $\pm 15$	11 $\pm 8$	17 $\pm 7$	12.3 $\pm 2.7$	8.5 $\pm 2$	76 $\pm 11$	81 $\pm 10$
BL > 180 m $\sigma_w^2 < 0.5$	51 $\pm 28$	26 $\pm 19$	5 $\pm 7$	13 $\pm 7$	10.9 $\pm 2.3$	7.7 $\pm 1.8$	81 $\pm 10$	84 $\pm 9$
BL > 180 m $\sigma_w^2 > 0.5$	28 $\pm 20$	19 $\pm 12$	14 $\pm 7$	18 $\pm 6$	13.0 $\pm 2.7$	8.9 $\pm 2$	73 $\pm 10$	80 $\pm 10$
$\sigma_w^2 < 0.5$	74 $\pm 57$	25 $\pm 18$	3 $\pm 6$	14 $\pm 7$	10.2 $\pm 2.4$	7.7 $\pm 1.8$	82 $\pm 10$	82 $\pm 9$
$0.5 < \sigma_w^2 < 1.0$	30 $\pm 22$	20 $\pm 12$	13 $\pm 8$	18 $\pm 6$	11.9 $\pm 2.5$	8.8 $\pm 1.8$	76 $\pm 10$	80 $\pm 10$
$\sigma_w^2 > 1.0$	16 $\pm 10$	10 $\pm 6$	21 $\pm 6$	25 $\pm 6$	13.0 $\pm 3.8$	8.9 $\pm 2.9$	73 $\pm 13$	80 $\pm 12$

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**Fig. 1.** Map showing sampling site locations. Inset map shows general location within central London.

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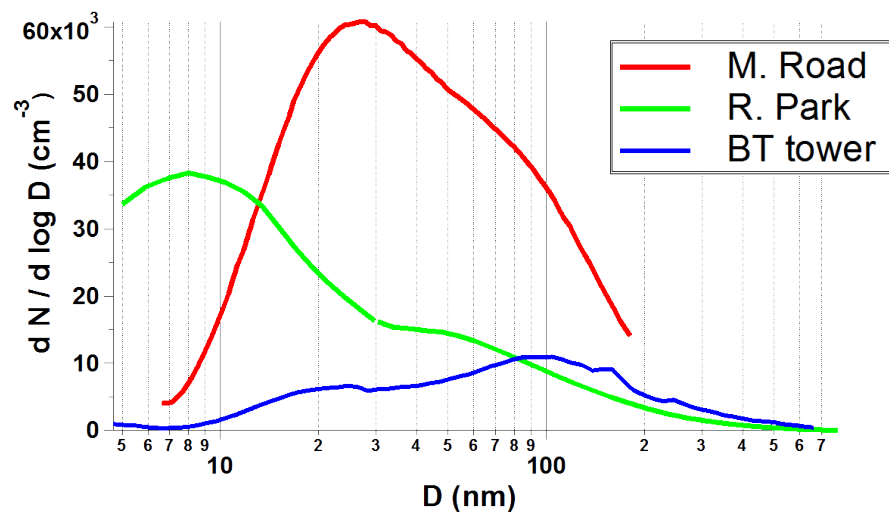
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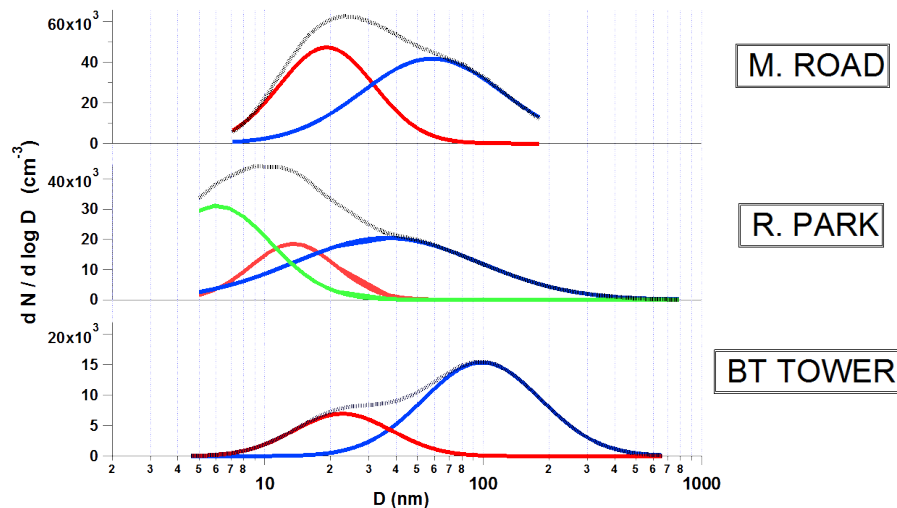


**Fig. 3.** Average particle size distributions (mobility diameter, nm) at Marylebone Road, Regents Park and BT Tower.

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**Fig. 4.** Measured size distributions from Fig. 3 expressed as combinations of component log normal distributions. Please note different y-axes for the 3 different sites (60, 40 and 20 000 cm<sup>-3</sup> for M. Road, R. Park and BT Tower, respectively).

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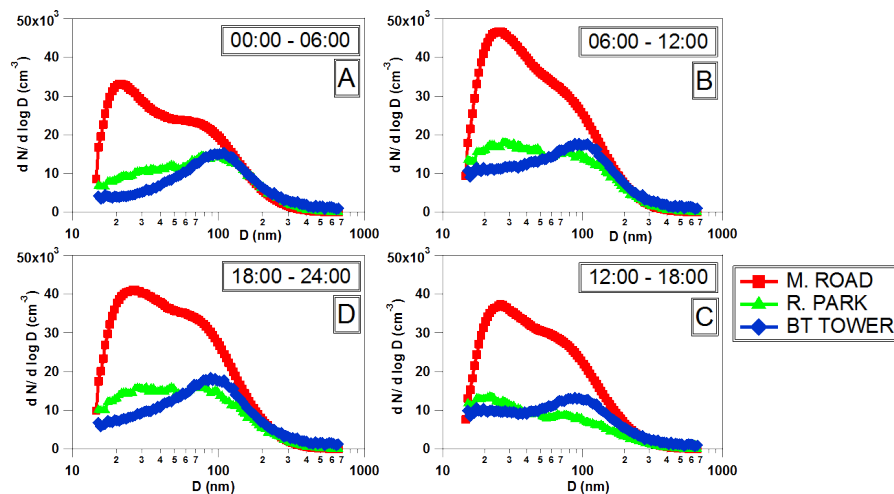
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**Fig. 5.** Average SMPS size distributions for 3 different sites (MR, R. Park and BT Tower) taken simultaneously during the REPARTEE-II field study. Data are average for the 6 h time period at 00:00–06:00 (A), 06:00–12:00 (B), 12:00–18:00 (C) and 18:00–24:00 (D).

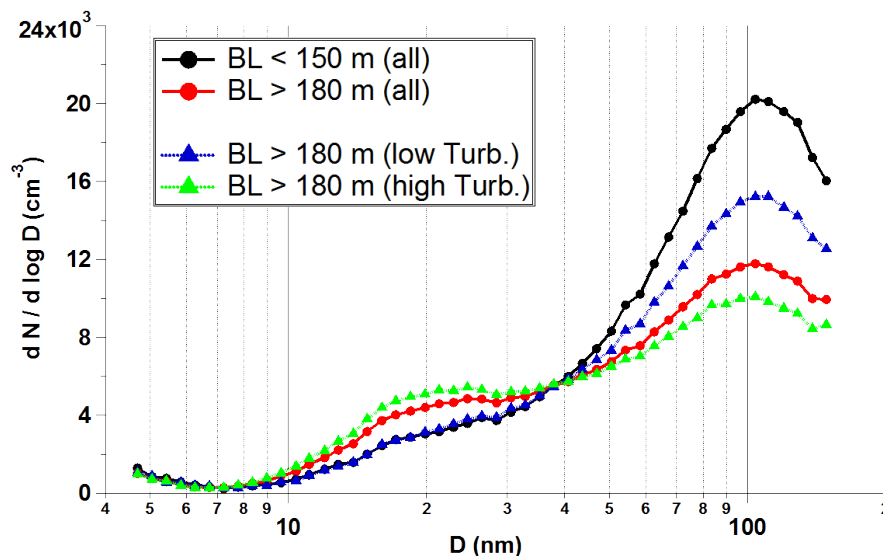




**Fig. 6.** Same size distributions as in Fig. 5, re-drawn for comparison. Average SMPS size distributions taken simultaneously during the REPARTEE-II field study at 6 h time period at 00:00–06:00, 06:00–12:00, 12:00–18:00 and 18:00–24:00 for **(A)** MR, **(B)** R. Park and **(C)** BT Tower.

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**Fig. 7.** Average nano-SMPS size distributions at the BT Tower site (BT Tower) for periods of: UBL height below the BT Tower tower sampling height (<150 m); high UBL height (>180 m); low  $\sigma_w^2$  (<0.5 m<sup>2</sup> s<sup>-2</sup>) and high  $\sigma_w^2$  (>0.5 m<sup>2</sup> s<sup>-2</sup>). Measurements of UBL height and  $\sigma_w^2$  were derived from the Lidar.

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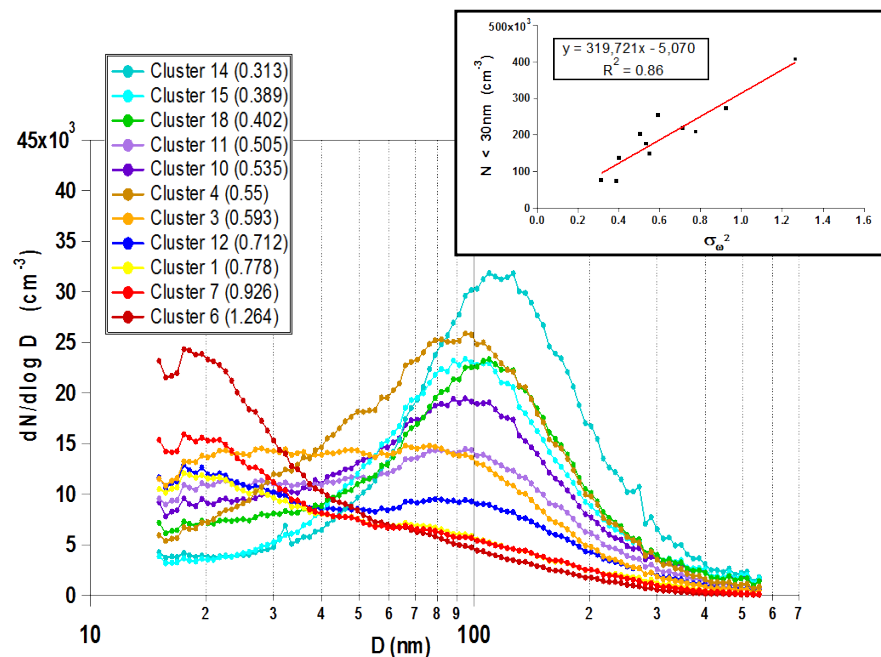
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**Fig. 8.** SMPS cluster analysis from the BT Tower site. For each of the 11 clusters reported, in the legend an average value of  $\sigma_w^2$  ( $\text{m}^2 \text{s}^{-2}$ ) obtained with the Lidar is given.

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