

# REMARKABLE DYNAMICS OF NANOPARTICLES IN THE URBAN ATMOSPHERE

## RESPONSE TO REVIEWERS

*Replies to Referees in bold italics*

### **Anonymous Referee #1**

Received and published: 10 February 2011

The paper shows interesting aerosol size distributions measured at different sites in London, a shift in the size distribution are sometimes found, this can be due to a semivolatile fraction. To be sure that other processes do not transform the particles, more careful analyze of data should be done.

***Reviewer #1 raises a number of questions which we welcome in order to improve the quality of this manuscript.***

Major issues

(1) Instruments. It is too difficult to remember the different cuts for the CPCs, it is better to write out diameters e.g for  $D_p > 7\text{nm}$  or  $D_p > 2.5\text{nm}$  both in text and Figure 2.

***A new table has been constructed to make this information easily available, and figures are also included in the text.***

Table 1 is unclear, what is nano and what is normal, use models and diameters instead. Include also the different CPCs in the table.

***Done in the new table***

Are two CPC running at each site, one for the DMPS/SMPS system and one for the total?

***Yes, and a list of all the instruments is now included in a major table***

In 2.2 The CPC in R. Park has a cut of 2.5 nm  $D_p$  and in 2.4 the SPMS at Marylebone Road has a CPC with a cut of 2.5 nm  $D_p$ , do you have any data for total number concentration for the CPC at Marylebone Road, for comparison with R. Park? For the R. Park, you can look at the difference between the two CPCs, for the size interval 2.5-7 nm  $D_p$ , and see how/if this size interval shifts over the day, if new particle formation occur you can also see an increase in the number concentration.

*The number of instruments used for this study may have led the referee to misunderstand the availability of the instruments at each site and we apologise for this. We have now listed all the instruments in a new Table 1. We did not have CPC counts for M. Road for either of REPARTEE I or II and we did not have any CPC for RP during the REPARTEE II experiment. The reason for that is that all the CPC were used to deploy with DMAs during REPARTEE II in order to simultaneously deploy 3 SMPS system during the month of October 2007.*

(2) More meteorology data has to be included. Can you see different size distributions depending on wind direction? Both Barlow et al. (2010) and in Martin et al. (2008) show that westerly winds are most frequent, are the size distributions in R. Park and at BT Tower changing depending on wind direction?

*The current paper already has a large number of figures and it focuses on particle number distributions. We did not find any systematic variation with air masses or wind direction, presumably as the distributions are dominated by city-wide emissions.*

*The analysis presented in Figure 8 for size distributions on the BT Tower includes data from all wind directions and still generates an  $R^2$  value of 0.86, strongly suggesting that wind direction is not an important factor in determining nanoparticle numbers.*

Is it possible to use data from only the south sector for R. Park in Fig 3, 5 and 6, to be sure that the sampled aerosol is traffic related?

*We did not find any difference by selecting different wind directions, possibly because southerly wind directions were characterized by higher wind speeds which consequently reduced the general aerosol particle number concentration across all size ranges. We also did not find any major difference for weekdays versus weekends (see below).*

Martin et al. (2008) show that during the 2006 campaign the mean temperature was over 15 degrees Celsius, which is higher than during 2007, can the size distribution in R. Park been influenced by temperature?

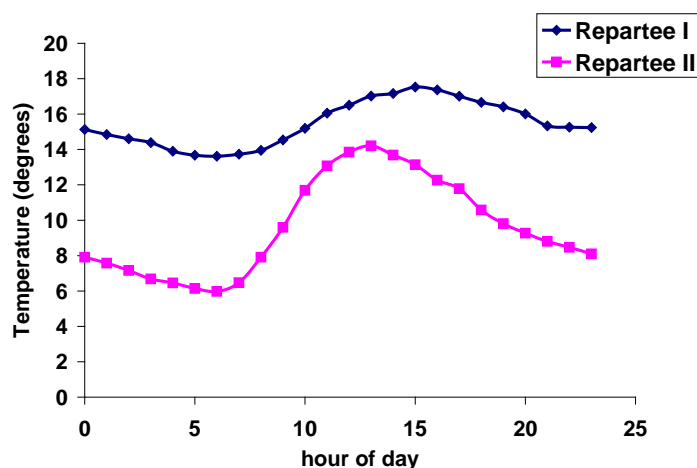
*The average conditions for the two campaigns appear below:*

	Repartee I	Repartee 2
Temp (R. Park) (°)	15.5±2	10.4±3
RH (R. Park) (%)	79±10	79±12
Temp (BT Tower) (°)	12.3±1.7	7.7±1.9
RH (BT Tower) (%)	84±9	79±11

*Warmer conditions were found for REPARTEE I relative to REPARTEE II. Temperature will undoubtedly influence particle evaporation processes.*

On page 30665 line 24: the shift to smaller size in the park is during the warm part of the day. How large is temperature difference during the day?

*We present a chart below where we show the diurnal variation of the temperature profile at the R. Park site during the REPARTEE II campaigns. The average temperature range in REPARTEE II was 8°C for hourly data.*



Can the particles easily be transported into the park with horizontal winds, how many trees are growing in the park, they will influence the deposition, the trees can also be a source for volatile compounds, have you seen new particle formation in the park?

*The Regents Park is fairly large (the second biggest of the city of London). Some more information can be found at: <http://www.royalparks.gov.uk/The-Regents-Park.aspx>. The 487 acre (about 2 km<sup>2</sup>) park is mainly open parkland. Meteorological, gas-phase and aerosol measurements were conducted from the top of a 10 m high tower constructed on site. To minimize sampling losses, air was drawn down a vertical sample pipe approximately 150 mm in diameter, which allowed air to be drawn from above the surrounding tree line. Air was sub-sampled from the main sample flow in an iso-kinetic manner through a 40 mm diameter stainless steel pipe with a knife edge forward facing tip, and was taken via a gentle 90° bend into the air conditioned mobile laboratory (Dall'Osto et al. 2009a,b).*

*We saw no evidence of nucleation (new particle formation) in the Park as judged from the diurnal pattern of particle number and size distributions. Furthermore, high*

*particle number concentration were accompanied by high concentrations of NO<sub>x</sub> and black carbon, indicative of a road traffic source.*

Can you use the stability data in Barlow et al. (2010), you say that the Lidar is a surrogate for the turbulence strength?

*$\sigma_w^2$  is the variance of the vertical wind velocity ( $m^2 s^{-2}$ ), and we use  $\sigma_w^2$  (taken at the lidar height interval 100-250 m, i.e. around the sampling height on the tower) measured by Barlow et al. which can be used as a surrogate of turbulence.*

Rain frequency during campaign, are the hours with rain sorted out? Are any data sorted out?

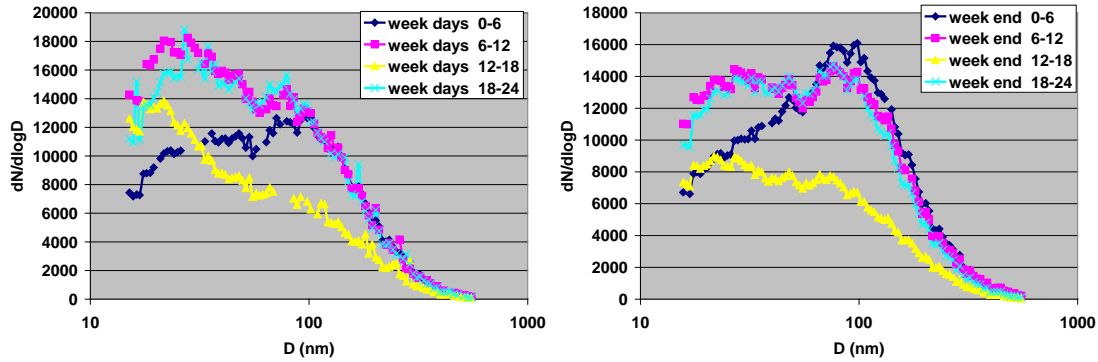
*A number of light precipitation events were recorded during REPARTEE I (especially during the second part of the field study; 18<sup>th</sup>-26<sup>th</sup> October 2006) whilst only a couple of events were observed during REPARTEE II (28<sup>th</sup> October and 8<sup>th</sup> November 2009). A reduction of PM was noticed as expected during the rain events, but no variation was seen on the overall dataset between including or excluding the rain events.*

How large is the long range transport of accumulation mode particles into London, is this transport depending on wind direction?

*During the REPARTEE I experiment we found increases in accumulation mode particles due to long range transport of pollutants from continental Europe. During these events, the typical wind direction was easterly.*

(3) Traffic related questions. Martin et al. (2008) saw differences in emission between weekdays versus weekends, are the size distribution in R. Park changing due to this? Are all days included in the averages shown?

*All days are included in the analysis as stated in the paper. If data starts to be removed and filtered, this work would become more a case-study than a systematic one. However, we present below aerosol size distributions for REPARTEE II for R. Park in order to provide additional information for Reviewer 1.*



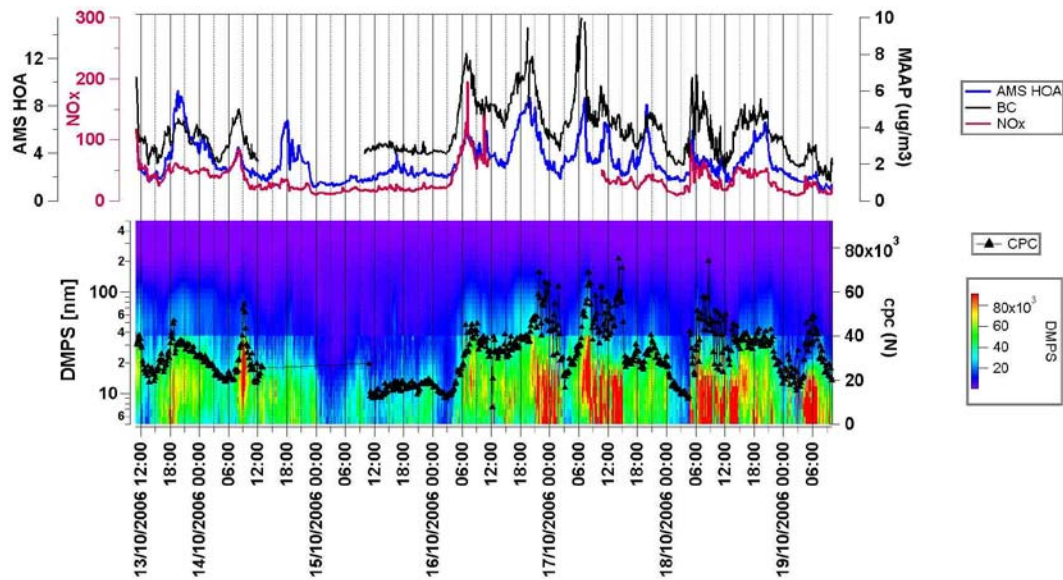
*The general trend supporting the evaporation of particles can be seen for both week days (WD) and weekends (WE). Specifically in the R. Park, more small particles can be seen during the period 12:00 to 18:00 for the WD relative to the WE period.*

Are people having barbeque in the park during weekends?

*Barbeques and fires are severely forbidden at all the Royal Parks of London and management people are always circulating around the Park to make sure all the rules are followed. Moreover, several scientists were spending many hours there during most of the field study (weekend included) and no one noticed any local fire. The ATOFMS did not detect any biomass burning spikes.*

Would be interesting to see a figure with the size distribution as a function of time (with concentration in colors), to see how the 10 nm mode in the Park change over time.

*We report below the DMPS (3-800nm) measurements taken in 2006 at R. Park along with BC (MAAP), NO<sub>x</sub> gas and primary organic aerosol (HOA) measurements taken with the AMS along with the TSI CPC 3776 (>2.5nm) for the period 13-20<sup>th</sup> October 2006 as an example.*



Paragraph 3.2 page 30666 line 17 starting with 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 The emissions of particles from the city are much less during night depending on less traffic, even if the M Road has dense traffic during the night, the traffic in London is reduced.

*The text has been amended to draw the reader's attention also to the plot in Figure 6(a) for M. Road which reflects the point made by the reviewer.*

(4) On several places it is stated that the shift in particles size cannot be due to dispersion, this has to be more carefully discussed, both the dry deposition in the street canyon and the effect of mixing can be large for the 20-30 nm particles (as many of the references has seen when they have modeled the urban aerosol).

*The effect of dispersion and mixing for all particles in the size range between 10 and 40 nm is similar. The deposition velocity is greater for 10 nm particles than 30 nm particles which would tend to increase the mode of the size distribution during atmospheric transport. Since we see a reduction in the mode, we attribute the shift in particle size to evaporation processes.*

(5) Paragraph 3.3. It is difficult to follow the paragraph with the combination of Lidar, SMPS, and NOX measurements, it has to be rewritten. E.g. in Barlow et al. (2010), three heights are defined, ZBL, ZAER, and ZMH, this has to better be clarified. Is BL in the text one more height defined?

*Barlow et al. refer to:*

*$Z_{BL}$  = boundary layer top*

*$Z_{AER}$  = aerosol layer depth*

*$Z_{MH}$  = mixing height*

*Aerosol layer depth ( $Z_{AER}$ ) - this is calculated using the gradient in the backscatter measurement, and is detected as the first large gradient in backscatter we see going up from the surface. As the backscatter is a good proxy measurement for the concentration of aerosol, this essentially shows us the depth of the aerosol layer adjacent to the ground. This is most useful at night when the lack of convection and increased humidity allow denser layers of aerosol to develop, associated with the nocturnal stable layer.*

*Boundary layer top ( $Z_{BL}$ ) - again calculated from the gradient in the backscatter, but this time calculated from the top of the lidar measurements downwards. This basically finds the limit to which the lidar measures backscatter, which again we assume is equivalent to aerosol. On a clear (i.e. non-cloudy) day this will show the top of the 'entire' boundary layer i.e. somewhere in the entrainment zone between the cleaner troposphere and the more polluted boundary layer below. If clouds are present then this height should be ignored; clouds rapidly attenuate the lidar signal and this height will be roughly a few tens of metres above the cloud base, depending on how thick the cloud is.*

*Convective mixing layer height ( $Z_{MH}$ ) - this is calculated using a threshold on the value of the vertical velocity variance. As mentioned above, the variance gives us a measure of the intensity of the vertical turbulence occurring, which is dominated by convection during the day. To calculate the height we look at profiles of the variance from the ground up; if the value of the variance is above our threshold (in this case  $> 0.2 \text{ m}^2 \text{ s}^{-2}$ ), then we assume that convection is mixing air from near the surface up to this height. The point at which the variance drops below the threshold we assume to be the top of this mixing layer.*

*In our work we use the  $Z_{MH}$  for Figure 7 and the mean variance of the vertical wind velocity ( $\sigma_w^2$ ) between 100-250 metres for Figure 8. The text on page 30667 and legend to Figure 7 have been amended to clarify this point.*

Difficult to understand that the increased accumulation mode can be due to long range transport, Barlow et al. (2010) can not see long rang transport.

*Barlow et al. (2010) did not report a detailed study on differences due to long range transport. We clearly see changes in concentrations of sulphate and nitrate attributable to long-range transport (see Dall'Osto et al., 2009, now cited in paper).*

Line 20 page 30668 . . .lifetime of surface-derived sub-50nm particles is short compared to that of NO<sub>x</sub> and larger particles, Yes, this is true, but can also be due to high dry deposition velocity for sub-50nm particles

*It is anticipated that dry deposition is unlikely to impact significantly on the upward vertical transfer of pollutants due to lack of contact with surfaces.*

Minor issues

Fig.2 In text REPARTEE I, but paragraph 2.2 says REPARTEE II

***Corrected***

Page 30666 line 21 Martin et al. (2009) measured total particle number flux, should be Martin et al. (2009) measured particle number flux for DP > 10 nm

***Corrected***

Page 30672 line 17 have totally failed to account for their semi-volatility (Gidhagen et al., 2005; Clarke et al., 2004). Better to write something like the effect of the semivolatility has not been considered.

***Corrected!***

Page 30673 1 line 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). No, Barlow et al. (2010) show 10 minutes for high turbulence and 20-50 minutes for more stable conditions.

*The reviewer is correct (Barlow revised her estimate from the first draft of her paper) and this has been amended.*

### **Anonymous Referee #2**

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The paper is a nice compilation of data showing that evaporation is a plausible reason for the different particle size distributions measured at different sites. This has been discussed for a while, but I have seen no data showing this, even though simple calculations have shown that it is highly probable.



*We thank reviewer #2 for the appreciation of this work*

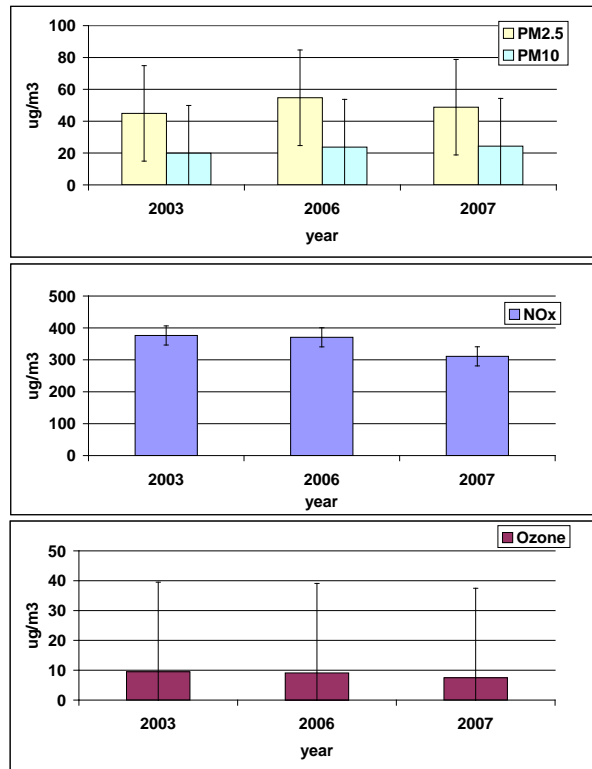
1. The data upon where the paper is based is from different sites and different times, thus this would be much easier to follow if both the sites and the equipment used at each site. Either one big table or two smaller. This also makes the authors aware that all information is not in the text, e.g. the traffic at each site. a. Suggestion for Table-headings in section 2.1: site, site description, height over ground, traffic count, Comment b. Suggestion for Table-headings in section 2.3.1: site, time frame (e.g. Oct 2003), time resolution (4min30sec scan), equipment (SMPS, CPC etc) and comment (reference or campaign name etc)

*A new table is now incorporated*

2. Please use descriptive names, e.g. M. Road instead of MR, and the same name throughout both text and figures.

*Corrected. All the names are now: R. Park, BT Tower and M. Road*

3. Section 2.3 was there big differences between the Octobers by pollution level, weather, traffic etc? Might be nice to add a table on these numbers for the reader to make his/her own opinion.



*We report above the measurements taken at the M. Road site for the year 2003, 2006 and 2007, where we can see for most pollutants the difference is minimal.*

4. Organic carbon???

*Organic carbon data in Table 2 are not directly relevant to the interpretation of size distributions and have been deleted.*

5. Nano particle evolution: the data used to support the insight that the “dilution” of ultrafines is larger than the dilution of PM10 or EC is not worked through; the EC in the park and the tower is related through regression and the pm10 by a ratio. The particle number on the other hand is related between different sites (Kensington and Tower). This does put extra doubt that this data really supports the conclusion. Maybe this can be calculated somehow. Needs further discussion or data!

*Minor amendments have been made. The regression of EC concentrations is included to demonstrate the close correlation of ground-level concentrations across central London. The ratio data in Table 2 are sufficient to demonstrate a loss of particles relative to EC at the BT Tower site relative to the ground-level North Kensington and Regents Park sites.*

6. Page 30664, line 7, “A second independent study,” seem to refer to “The part of this study described in section 2.4,”

*Corrected.*