Anonymous Referee #1

Received and published: 11 September 2012

The manuscript presents results from several different stations in and around the metropolitan area of Barcelona, Spain over a period of about one month. The main data presented are total particle number concentrations, number size distributions and black carbon concentrations, which are used to estimate the main sources of particles in the area, distinguishing between regional and urban/traffic production. The extent of the concurrent measurements is very impressive, and the data would merit publication in ACP. However, I have a few major concerns relating to the interpretation and presentation of the results that the authors need to address first. If they can do this, the manuscript can be considered for ACP. Detailed comments below.

We thank referee 1 for appreciating the present manuscript and for finding the extent of the concurrent measurements very impressive. We answer the comments in italic.

Major comments

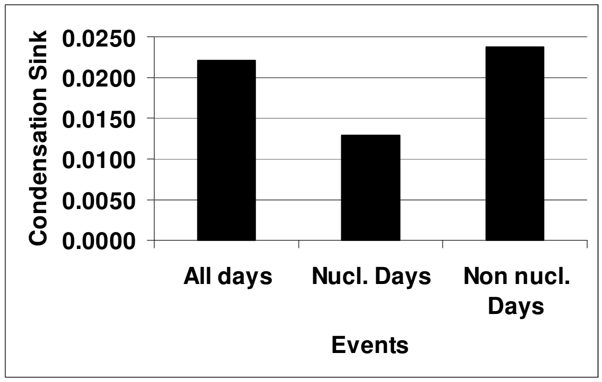
Data interpretation:

While the analysis of the presented data set is certainly challenging, I find that the authors have in some cases oversimplified and over interpreted the data. My main concerns are listed below.

1. Event analysis.

While it is a pity that only one station had available SMPS data for the reported regional event, the data seem convincing. I would like to see a plot of the condensation sink (CS) during the measurement period. By looking at Fig. S3, the CS seems to be lower than normal during both the reported regional and urban events. Currently the CS is only discussed in a qualitative way.

The referee is correct in stating that only one SMPS was working for the regional nucleation of the 25th of September. However, we support such event with five additional CPC (2 in the TC, 2 in the TM and 1 in the UB) clearly showing this event is seen at all the monitoring sites. As requested, we calculated the condensation sink, and we report quantitative measurements (as summary in new Fig. 10). We also provide the chart below for the attention of the referee, and we report numbers in the paper.



We also include a new Figure (figure 10), following the pioneering study of Stanier et al. (2004), showing the CS as a function of UVxSO$_2$ *(Correlation showing UV * SO2 versus condensational sink for four different seasons. Condensational sink (y axis) is plotted against the product of ultraviolet light intensity and SO2 concentration (x axis), a proxy for sulfuric acid production). See later on in the text.*

The latter event which is reported to be an "urban“ event raises many questions for me. It is stated in the manuscript that in the afternoon the sea breeze causes the air to first pass over TM. Presumably the sampling there is then less influenced by the urban emissions than RS and UB. At least according to Fig. 1b, this seems to be the case. For the "urban“ event, the authors write that the event measured at TC and RB are transport from the urban area of Barcelona. If the wind direction is such that the air from Barcelona travels to RB, then I would expect that TM should not see much nucleation at all if the particles are formed in the city. Especially in the afternoon, the sea breeze should be causing cleaner marine air to impact TM, however, the highest particle number is seen at that time.

Figure S1 (picture of the city with the monitoring sites) shows that the TM site is at the on the edge of the city whereas the RS and the UB are more confined within the city centre. However, Figure 1 (diurnal profiles of N and BC) shows high levels of BC at the TM, as busy streets and a busy motorway are nearby. It is difficult to know how the concentrations of BC and N distribute across the urban area of Barcelona. We classify as urban region not only the city centre, but the urban area around the city (indeed for this event, the UB is a source of nucleating particles, which then increases in size before reaching the TC and then the RB). More to follow.

How is this situation possible if the particles are formed in the city? Are there WD data available to show in which direction the plume would be expected to move during the event?

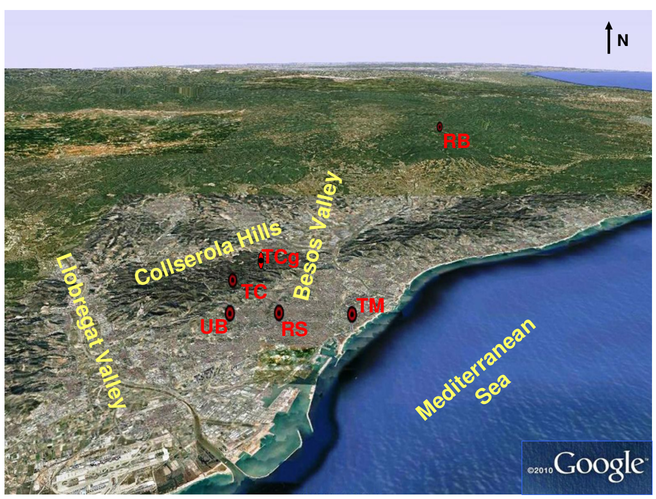
Wind direction shows a typical afternoon sea breeze with a WD of 150-200º. Again, the urban plume is likely to have a spatial distribution slightly larger than the city centre itself, due to dilution, dispersion and other minor sources located just outside the city centre. More to follow.

Even more importantly, the authors suggest nucleation occurring in the city, which would function as a point source. The non-growing modes at UB and RS would agree with this, but the growing modes at TC and RB suggest to me that something else is causing the particle production and growth.

Indeed the non growing mode of the RS and UB suggests the urban agglomerate as a source of secondary nucleating particles. The urban plume does not consist of particles only, but also of VOCs. We believe particles are growing while travelling away from their urban origin. We also include a better figure (see below).

But to keep with the idea of urban nucleation, the growth of the mode should be related to changes in available condensable vapors between nucleation (e.g. RS) and detection (e.g. RB), though this might be challenging. The change of the modal size at TC and RB should definitely not be directly interpreted as the GR of the nucleating particles, as done now, if the NPF is not assumed to be a regional event.

The secondary nucleation event begins in the urban area of the city of Barcelona, and continues to grow as the sea breeze (wind direction at 150-200º) transports the urban plume to the TC up to the Besos Valley reaching the RB site. The growth rate is calculated with the plume shown in old Figure 5 (now Figure 6): 15:00-16:30 at the UB, 16:30-18:00 at the TC and 18:00-19:30 at the RB. It is also important to note that the plume is no longer transported at the RB after about 20:00 where the sea breeze becomes weak and the RB is no longer linked to the city of Barcelona through the Besos Valley (see Figure below taken from the presenting overview SAPUSS paper of Dall'Osto et al. 2012).



The TCg, TC and RB sites are all aligned with the Barcelona city centre in a position to receive urban plumes from the city, especially in the afternoon when the sea breeze *arrives from the South-West encountering in order: TM, RS, UB (roughly together), then TCg-TC, and finally the RB.*

In summary, if the authors wish to show that this event was an urban event, they need to provide a self-consistent explanation of the area where particles would be produced, in which direction the wind transported the particles, and what do the growth rates need to be to explain the particle sizes observed at the different locations. E.g. why is the difference between UB and TC of the same order as the difference between TC and RB if the growth is 2-3 nm/h at both TC and RB? And how can there still be (growing) new particles visible at 23:00 in TC? That suggests to me that the particle production during this day was occurring in a larger area than just the city.

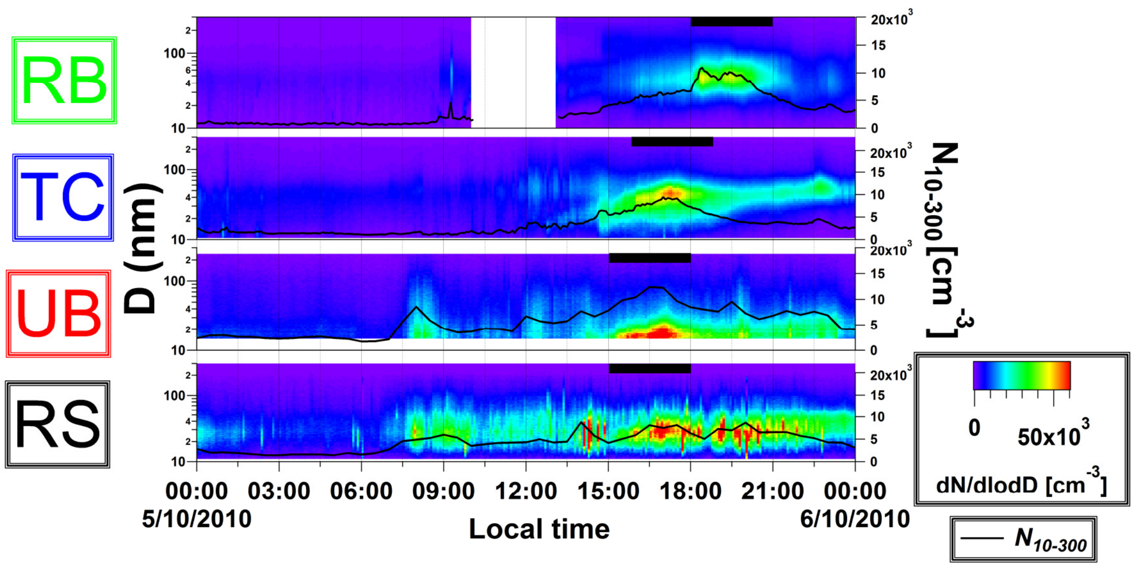
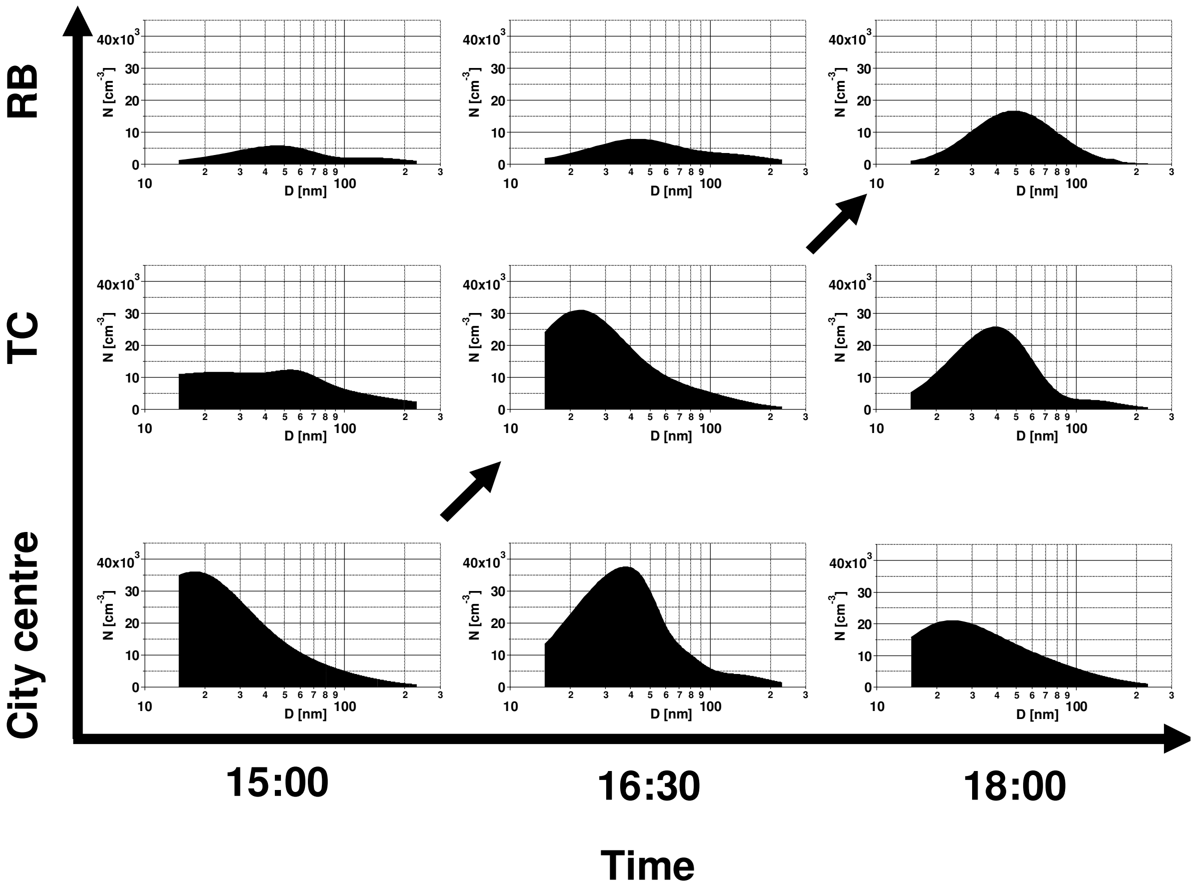


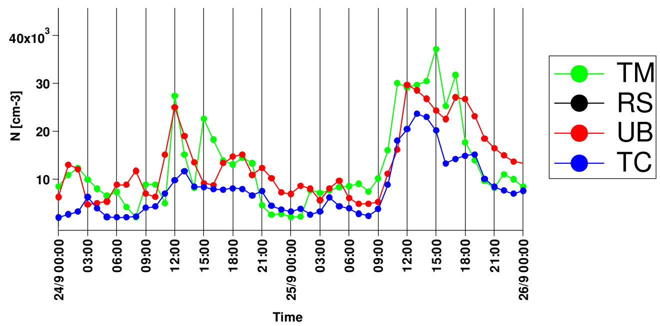
Figure 5 clearly shows that there is no particle production at the TC and even more importantly at the RB at around 15:00 when the urban nucleation event is occurring in the urban region of the city of Barcelona. We can therefore conclude it is not a regional event, but more of an urban nucleation event. Figure 5 (now Figure 6) also shows that the total SMPS particle number concentration did not increase simultaneously at all sites, hence reflecting more a "plume" condition rather than a regional event. In order to make this very clear, we made a new Figure to better explain this concept (and a black line showing where the main N of the urban plume is).



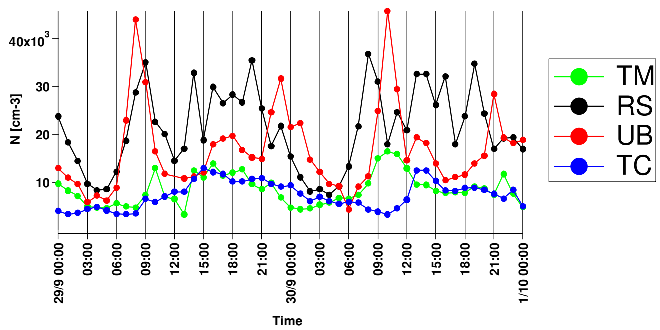
2. Vertical extent of particle formation.

The authors need to provide more evidence that the height of the TM and TC sites are more important than the geographical locations. Currently, small changes between TM/TC and RS/UB are interpreted to show changes in the vertical extent of particle production. Perhaps the authors have data to back these claims, but based only on the data shown, I would expect a much larger impact from the different locations in the inhomogeneous metropolitan area. Also used to show how particles are formed at higher levels, on page 16624, lines 10-16, the authors state that the points under discussion in Fig. 6 occurred on 3 days with possible NPF, and that particles were seen at the tower sites but not at ground level (UB and RS). When I look at the plots in the supplementary material, for RS CPC data is lacking for all three days, SMPS data for two of them. For the UB site, SMPS data is also lacking for the first two days, and for the third the SMPS shows a concentration and distribution similar to the "urban“ event. Furthermore, the CPC counts at UB according to Fig. S2 are the same or higher than for both TC and TM on all the three mentioned days!

We show two nucleation event days where there was clearly higher concentrations of N at the TM relative to the ground level (RS, UB). It is also important to stress such conditions were detected only at the urban tower (TM) but not on the background urban tower (TC). We compare the figure below (24th, 25th September, with maximum at 15:00) with higher particles at the TM site with two other non-nucleation days, clearly showing a different scenarios (higher N at ground level all the time, 29th, 30th September).



Nucleation days (higher N in the afternoon at the urban tower TM)

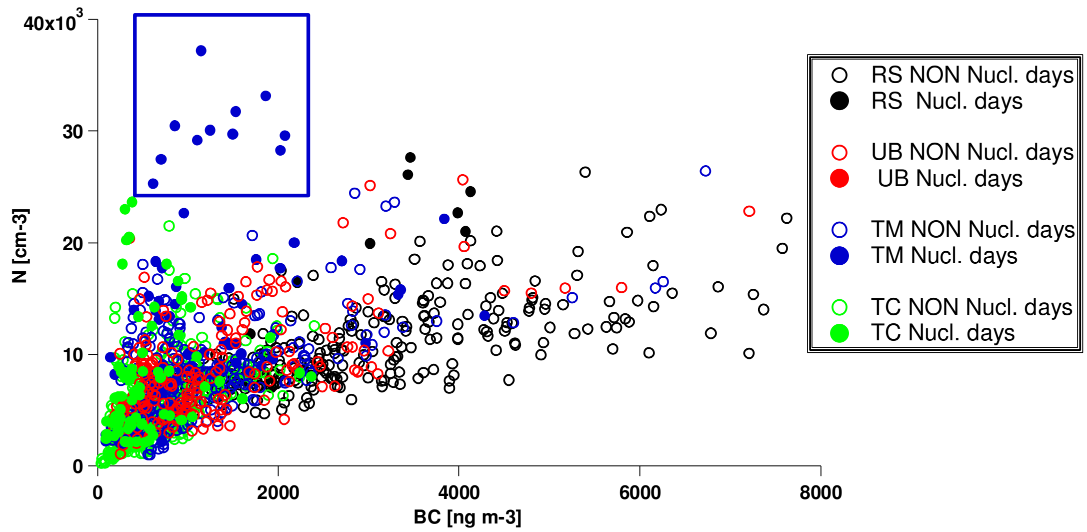


Non Nucleation days (higher N at ground level all the time)

Data from RS on 24th and 25th were not available, but it is likely that they would have been strongly influenced by local sources in the morning, and an enhancement in the afternoon due to nucleation. Actual figure 6 (old figure 5) shows that the urban nucleation event is more evident in the UB rather than in the RS, as local traffic does influence N and CS.

The authors need to clearly show how they came to the conclusion that NPF is only seen at tower level and not at ground level, as this would have been a very surprising observation since the tower sites themselves are not very high above ground and the boundary layer is expected to be relatively well-mixed.

We also report the N versus BC chart (hourly data, all hours) as a function of nucleation days versus non nucleation days, showing clearly a higher number of N for the TM for the former case (blue panel).



3. Interpretation of TM in Fig. 8.

The authors state in the text "leading us to suggest some particles may evaporate (leading to a lower N/BC) when the atmosphere starts to heat up in the morning. In other words, a reduction of the ratio N/BC (07:00–10:00 at TC and TM, Fig. 8) can be explained by some semi-volatile particles evaporating when the urban heat begins to develop. During afternoon, more particles are seen in both towers, higher than at the ground site. This is an indication that nucleation processes are taking place above the city in the afternoon at higher intensity than ground level." If I compare Fig. 8 to Fig. 1, the above text makes no sense. The reason for the large variation in N/BC is clearly due to changes in BC and not N, and there the BC trend seems consistent with the seabreeze behavior, decreasing in the afternoon. The particle number at TM never exceeds UB or RS in Fig. 1, yet the authors write that more particles are seen at TM and use this as an indication that particles are produced above the city!

New Figure 1 shows all the data for the field study. By contrast, when we look at specific days, we show very different diurnal profiles. For example, Figure 4 shows the diurnal variations of the particle number concentrations for (a) Urban nucleation event day on 5th October 2010 and (b) typical polluted day (29th September 2010) at four different monitoring sites. Clearly, the two situations are different. Whilst the particle number is higher at ground level during a polluted day (figure 4b of day 29th September, like figure 1 for all Field study). The variation of BC/N cannot only be explain for the changes in the BC, as we have shown in several Figures (see for example old Figure 6, new Figure 7) that there is a linearity between N and BC, but this does not apply during nucleation event days. Additionally, as reported in the text "A lower ratio is seen at TC and TM for the morning rush hour. This cannot be explained by dilution as when the boundary layer develops, both BC and N should dilute, leading us to suggest some particles may evaporate (leading to a lower N/BC) when the atmosphere starts to heat up in the *morning." If N increases with traffic(BC), then a lower N/BC implies less particles are emitted for a given BC concentration, hence suggesting " some semi-volatile particles evaporating when the urban heat begins to develop".*

Structure of the paper:

There are a lot references to other work in all sections of the manuscript. For introduction, methodology and discussion sections this is of course fine, but also the results and conclusions sections bring up results from other work, sometimes with unclear references, which makes it very confusing for the reader to be clear about which results are new and which old. As an example, while explaining results in the abstract, it is stated that "This is also evident in the urban background annual mean diurnal trend of N/BC, showing a midday peak in all seasons", making it sound like a result from this study, although the reported measurements only cover one month. The text should be clarified throughout the manuscript, so the reader can easily distinguish which results are from this study, and which are from already published work.

We reduced the number of references, and we put them in better context. Specifically, we made it clear what the novel aspect of this paper is.

Other comments:

Grammar: There were sections of the text that would benefit from a read-through of one of the native English speaking co-authors, and I recommend that the authors do this for any future versions of the manuscript.

Addressed

Abstract: I feel the abstract is longer than necessary. Some better restructuring of the paper and the main results could also lead to a more condensed abstract. Additionally, the abstract starts by saying that <100 nm particles were investigated, but later on concentrations up to 500nm are discussed.

We were asked to expand the abstract by the ACP editor at the beginning of the publishing process. However, we have tried to structure it better once again.

Page 16606, line 15 and page 16607, line 1: "Little is known about the vertical distribution of primary and secondary UF particles in the urban atmosphere" and later "Even less is known about the vertical distribution of secondary new UF particles, especially in the urban atmosphere."

Edited (remove primary and secondary from first sentence)

Title: I would recommend adding "in Barcelona, Spain" to the end of the current manuscript title.

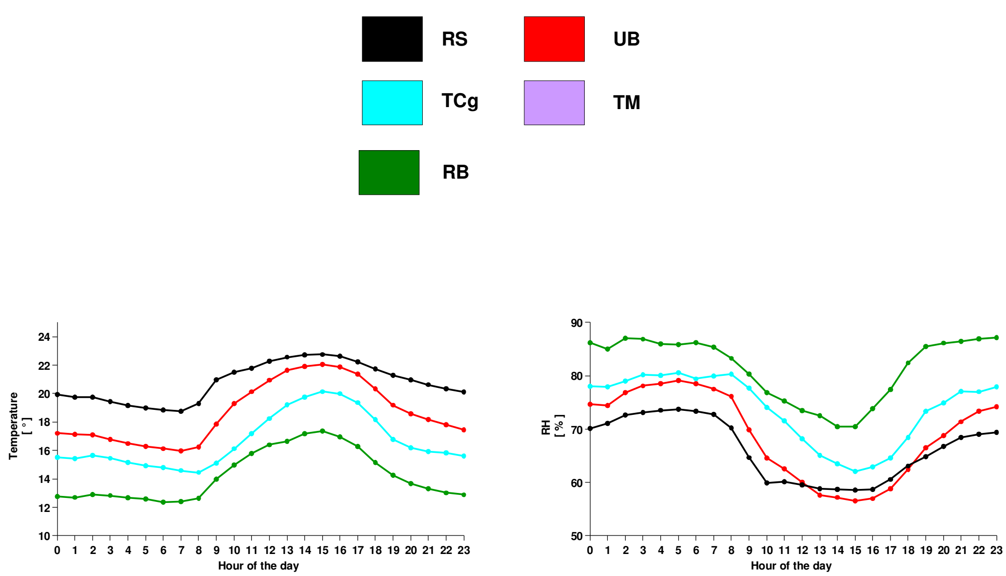
Added

16612, 2: Although certainly within the error bars, do not use "same order" when the order is not the same.

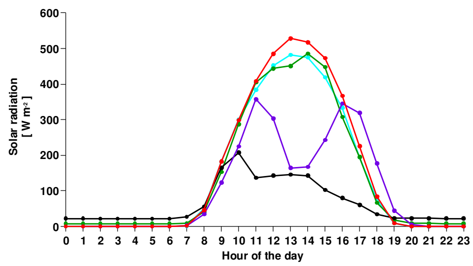
Removed "same order"

Fig. 6. There is speculation about the temperature effect on N/BC, but I would have assumed that if the higher N/BC ratio is due to nucleation, then radiation would be more important. The RS data set is the one that shows the best rainbow in Fig. 6C, but there is not much of a rainbow in Fig. 6d for RS, which is surprising. However, when I look more closely at Fig. 6d, the coloring of the points in RS seems to be completely different from the other three plots in 6d. Perhaps there was some mistake in the plotting?

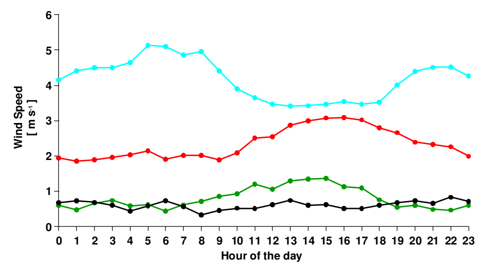
The problem over T and Radiation at the Road site derives from its street canyon features, as shown in the figure below (taken from the overview SAPUSS paper). We incorporate the text into the paper. The best rainbow for temperature in Figure 6c is probably reflecting an influence of temperature on primary vehicles emissions. The key message of Figure 6 is probably showing the linearity of BC with NO_x (Figure 6a), the dry conditions found during the nucleation events (RH, Figure 6b) associated also with strong solar radiation conditions (Figure 6d).



(a) (b)



(c)



(d)

Diurnal average Temperature (a), RH (b), Solar Radiation (c) and wind speed (d) at five different SAPUSS monitoring sites (From the SAPUSS overview paper, Dall'Osto et al., 2012)

Fig. 7: It is stated on page 16624, line 1 that the intercept is interpreted as the regional contribution, but as TC is much lower than the others, this cannot be true.

The intercept shows zero level of BC, hence theoretically indicating no presence of primary traffic emissions. The difference between the three more urban sites (RS, UB and TM, showing a very similar intercept) and the TC site may be due to an additional "urban" increment of the city. In other words, if TC is interpreted as regional contribution, then the higher values found for RS, UB and TM may be due to other non-traffic urban sources and or processes. We changed regional to non-traffic contribution. Moreover, later in the text we discuss the high variability of Figure 7, and we report additional figures S6 and S7. We thank the reviewer for making this concept clearer.

Table 2: The table says "cP air masses" twice.

Changed to……"day under polluted conditions (cP air masses) and diluted Atlantic conditions (mP air masses) at four different monitoring sites."

Fig 5.: The layout of this graph could probably be improved.

Improved, we report the 2d size distributions independently for each site rather than one figure. All Figures have been improved and changed.

Reviewer number Two
D. Westervelt (Referee)
dwesterv@andrew.cmu.edu
Received and published: 26 October 2012

This paper presents aerosol number and black carbon concentration data at several sites in Barcelona as part of the SAPUSS project. The authors identify three sources of ultrafine particles: traffic-related emissions, regional nucleation, and urban nucleation. Diurnal trends in N and BC were investigated and the nucleation events were explored in detail. N-BC correlations were presented to elucidate the contributing sources of ultrafine particles at each of the sites in and around Barcelona.

The authors have done a decent job at synthesizing a difficult and complex set of data, although I believe a few things should be clarified so that the overall "story" is more convincing. I recommend this paper to be published in ACP as soon as the changes are made.

We thank referee #2 for appreciating the present manuscript. We answer the comments in italics.

Technical comments:

P16604 L27-28: Secondary particles from the city center make up 61-71% of the total particle concentrations. But it only nucleated twice, and only one was urban. Is this 61% just for that nucleation day or averaged over the whole campaign?

It is for the whole campaign. It is correct that these would include other sources. We modified the text as: Our study suggests that the city centre is a source of both non-volatile traffic primary (29-39%) and other sources, including secondary freshly nucleated particles (up to 61-71%) at all sites.

P16605 L20-24: Some nomenclature confusion. For the second case of particles formed in the atmosphere after tailpipe emission, are you calling these primary? The description makes them sound like secondary particles, but then the next paragraph begins the secondary particle introduction. I wonder if you are referring to them as primary here because the vapors are low enough volatility and nucleate quickly enough to basically be treated as primary. Please clarify.

As discussed in Charron and Harrison (2003), "It is concluded that this size range contains freshly nucleated particles formed as the exhaust gases are diluted with ambient air". We refer these particles as "traffic" particles, formed by condensation in the diluting exhaust plume generally in the size range below 30 nm and formed as the hot exhaust gases are expelled from the tailpipe of a vehicle. We edited the text in order not to create confusion.

P16612 L2: This is not quite the same order in N as it is for BC. UB and TM seemed to be flipped, although within the uncertainty ranges.

UB and TM unfortunately are within the same range, as the large uncertainty does not allow to statistically consider them different.

Section 3.2.1 (Regional nuc): The authors mention the possibility of wrongly assigned nucleation events and go over the Dal Maso et al. (2005) criteria. Yet, in my opinion they are being somewhat loose with nucleation event assignment themselves for the regional event. It is possible that the events at UB, TC, or TM may not pass the Dal Maso criteria. Specifically, the appearance of 3-7nm particles satisfies the "nucleation burst" aspect but doesn't say much about their growth and survival outside of that range. I understand that the SMPSs were down at the other sites, which is unfortunate.

We included this discussion in the text, but given the appearance of 3-7 particles coincident with the beginning of the regional event, we can state this is a regional nucleation event. The referee is right in saying it is unfortunate the SMPS were down at other sites. However, the high values of N reported after the nucleation burst (after 11am) relative to other non nucleation days strongly suggest that this regional nucleation event was growing at all sites, hence reflecting the same conditions as the SMPS reported in Figure 3.

Section 3.2.2 (Urban nuc): I am not totally convinced that this is an urban event and not another (partially) regional event. First, if the winds blow from RS to UB to TC to RB, why does the mean particle diameter appear to be smaller at UB than RS (Fig 5)?

The referee is correct the wind blows from the UB-RS (city centre) to the TC and then to the RB monitoring site. The RS is a road site with a strong local influence, hence there is a contribution from primary traffic particles limiting the nucleation event. Particle concentrations are indeed higher in the afternoon relative to the morning (see figure 4), but not higher than at other sites, due to the higher condensation sink. This can also be seen in Figure 8 (low N/BC) and in the new figure 9. The RS size distribution of Figure 5 is affected by primary particles limiting the nucleation event, resulting in a lower particle number concentration relative to the UB (hence the mean particle diameter smaller at UB than RS). The larger nucleation mode seen at the RS (relative to the UB) is likely to be due to black carbon fresh traffic related particles.

Second, also looking at Fig. 5, the particles measured at RS could plausibly be emitted (20-40nm) and not secondary in nature. Finally, why does the mode continue to grow at TC until the end of the day and not at RB?

A fraction of the particles seen at the RS site are indeed primarily emitted, see previous answer above. The mode continues to grow at the TC but not at the RB because in the late afternoon the sea breeze becomes weaker, hence impeding the urban plume to reach the RB site throughout the Besos valley (see figure on page 3 of this answer to reviewers).

P16617 L3: I am not sure it is correct to call this the growth rate.

Modified to "monitor nucleation processes"

P16621 L12: Coagulational scavenging is referred to CS here, but earlier condensation sink was. CS is usually used for condensation sink. It is mentioned a few times that the low condensation sink above the city is partially responsible for the elevated number concentrations there (via nucleation). Could this be quantitatively shown and/or plotted?

Yes, we added values for the CS (see also plot above as answer from reviewer 1). Additionally, followed the pioneering work of Stanier et al (Stanier, C. O., Khlystov, A. ;Aerosol Sci. Tech., 38, 253–264, 2004) we plotted the CS versus SO_2 x UV, showing a key summary of all the different types of events we show during the SAPUSS experiment (Figure 10).

*Taking the same approach used by Stanier et al. (2004), Fig. 10 summarises our findings by showing the correlation between the product of [UV intensity * SO2 concentration] (a proxy for sulfuric acid production) versus the condensational sink calculated for four different monitoring sites (RS: black; UB: red; TCg: blue; RB: green). The empty dots correspond to periods when a nucleation event is not observed. The regional nucleation events are shown with triangle markers (regional nucleation, 25/09/2010) and square markers (regional background nucleation only, 17/10/2010). By contrast, the urban nucleation event (05/10/2010) is shown with full dots. The 45 degree line roughly divides each plot into two regions - the upper left region where nucleation is generally observed in urban areas (blue, red and black - TC, UB, RS), and the lower right region where nucleation is more common in the regional background area (green points, RB). The conclusions that can be drawn from comparing the different nucleation events presented in Fig. 10 are as follows: for a given level of pre-existing aerosol surface area (CS) and a given level of solar irradiance (UV), nucleation events occurring in the urban area require a lower level of SO2 concentration than events occurring in a regional background area. Hence, additional factors such as traffic organic compounds are likely to be involved in the nucleation events originating in urban areas.*

Grammar and writing style:

The whole manuscript could use several good proofreads before publishing. I found a few typos:

Edited them all, and checked again

P16605 L9: "...UF, the main component of ambient particles by number..." is a superfluous line since the same thing is said one sentence prior ("UF...make a dominant contribution to urban total particle number concentrations.")

Removed

P16607 L2: "NFP"

Edited

P16608 L15 "UCT"

Edited

P16613 L9: "air masses scenarios" This is probably not an exhaustive list.

We expanded briefly the description, although more information can be found in the presenting SAPUSS overview paper.

Presentation style:

The figures could use a little editing:

Throughout: use superscripts, not "cm-3"

Edited

Fig 1: Is the BC really in nanograms per cubic centimeter? Everywhere else is per cubic meter.

Edited

Fig 2: Is there a lower error bar on these? If so, they are blending in with the value bars themselves

Edited

Fig 3: It is odd to start with (a) at the bottom of the figure. Please fix.

Edited

Fig 5: Text looks stretched

Figure 5 made new

Fig 6: In print, this figure is very difficult to decipher. The colored points appear as almost all black because of their small size and black outline. Enhancing the PDF by a few hundred percent helps, but this is not ideal. I would suggest breaking up into separate figures or putting some in the supplement.

Edited