

Replies to referees

Referee #1

General Comments

R.1. This manuscript provides valuable information about the size distributions of submicron and especially ultrafine particles in Barcelona, describing the patterns and the dynamics when moving from the urban center to suburban areas and focusing on the emissions from vehicles. The manuscript is well written and describes the summarized size distributions around a Mediterranean urban center and it should be published after some minor revisions.

R. We thank a lot the comments and we celebrate that the referee thinks there are merits to be published.

R.1. A first general comment would be that the section 3.1 is unnecessarily too long, all the information contained are summarized in Tables 1-4. Instead of describing in detail all the elements of the Tables, a single paragraph highlighting the most interesting features should be compiled.

R. We agree that figures 1-4 are self-explanatory – and we keep the text as short as we could. Please note that only key variables in the text are discussed.

R.1. It would be most useful for the reader to add two maps in the manuscript illustrating the locations of the monitoring sites and the main trajectories described.

R. This is a large scale field study published in a special issue. We have agreed with SAPUSS ACP editors to use an introduction paper with all sites and maps of SAPUSS. Please refer to the SAPUSS overview for a detailed description of the sites and their locations.

R.1. Additionally, the paragraph 4.3 should be improved and expand the analysis. The contribution (or not) of new particle formation processes in the number concentrations reported are not explained in detail, since there are only three events observed during the period under study, perhaps it would be interesting to study explicitly these events.

R. An in depth study of the new particle formation events during SAPUSS can be found at Dall'Osto2013a. We added to the text that for detailed analysis this paper should be read.

R.1. Finally, in the same paragraph, except of a weak correlation to RH, practically no other correlation is illustrated to meteorological parameters. It would be interested to investigate more the breeze effect by examining wind speed and direction.

R. Paragraphs 4.3 is related mainly to the effect of primary traffic particles (see Figure S5). A very detailed description of meteorological data affecting nucleation processes can be found in Dall'Osto et al. (2013a). Note that Dall'Osto et al. (2013a) considered mainly particle number concentrations and BC, whereas this is a complete study on 4 SMPS deployed simultaneously – a novel concept not published so far in the literature.

Specific Comments

R.1. Page 27394, line 13: In Fig.2, Fig2a is the legend. All the references hereafter in the text to Figure 2 have to be corrected.

R. This has been corrected

R.1. Page 27394, line 16: What are the limitations of averaging over an hour time period?The transformation and evolution of size distributions within an urban environment can be very fast. Reducing the averaging period to the half, or even to a quarter of an hour, may give additional information especially when talking about transport and transformation between the monitoring stations with an Eulerian approach.

R. Our experience and the one of similar papers (see Beddows et al., 2009, Dall'Osto et al., 2011a and 2012) shows that one hour is enough to obtain the clustering separation.

R.1. Page 27398, line 16: *The maximum occurrence for Traffic-2 is during the night, probably with maximum values at midnight. Therefore it is not associated to rush hours, rather heating or cooking activities in the urban area could result to such trend. On the other hand, Traffic-1 looks as if follows the daily traffic patterns.*

R. Levels of BC, CO, SO₂, NO₂ and NO_x for cluster Traffic-2 are similar to the cluster Traffic-1, and high compared to others as can be seen in Figure S2. 97% of heating systems in Barcelona are working with Natural Gas, coal is not used, then BC is arising mostly from traffic. Also, the majority of the counts over the diurnal trend are seen during day time, reflecting the rush hour. Most importantly, Figure 4 clearly shows that Traffic-2 well belongs to the traffic group on the top right of the graph.

R.1. Page 27399, line 12: *Traffic-3 cluster is probably affected by photochemical processes, it has the second more intense solar radiation association after the NU cluster.*

R. The cluster Traffic-3 occurs during daytime, when the solar radiation is more intense, the boundary layer is fully developed and aerosol transport to the sites is most favoured. The diurnal trend for Traffic-3 and Nucleation clusters is different (see Figure 2d and 2h), especially for the UB site, the most affected by traffic emissions. Moreover, concentrations of traffic pollutants such as NO and NO₂ are higher for the Traffic-3 cluster than for Nucleation, and are also similar to the other traffic clusters (Traffic-1 and Traffic-2). Also, Traffic-3 is located at the upper right side of the graphs of Figure 4a-d, among the other traffic clusters.

R.1. Page 27400, line 6: *RB percentage is 15 % in the table. There are several places in the manuscript that the numbers are inconsistent to those of the tables.*

R. This has been revised and corrected.

R.1. Page 27401, line 4: *In supplementary material (Figure S2.j) for NU cluster at UB station high CO values are observed, the second after Traffic- 3. How do you explain these levels, is it possible that in the clustering process, traffic sources are mistreated as nucleation? What about BC values, they are not available in Table 2 for UB for thiscluster even if it is available for the other clusters. What is the availability of these data? In this cluster also PM10, PM2.5, N are really high as well.*

R. The UB site is influenced by the nearby busy Diagonal Avenue and therefore shows high levels of gaseous pollutants. However, except for CO, all other pollutants (NO, NO₂, NO_x, SO₂ and PM_x) show the lowest levels of all clusters measured at the UB site. Moreover, N_{15-30nm} is the highest for all clusters; therefore we don't believe traffic sources are being mistreated as nucleation in this case. The availability of BC measurements at the UB site was 35% and unfortunately there were no BC measurements available when the NU cluster occurred.

R.1. Page 27401, line 6: *The authors report a nucleation size mode at 14nm. However their harmonized dataset has a lower size bin at 15 nm. How was the calculation made, what dataset was used and is it valid after all to report a mean mode diameter outside the size range of the dataset used.*

R. The nucleation size mode was located at 15 nm, it was a mistake that has been corrected. The tool used was the multipeak fit of IGOR software.

R.1. Page 27404, line 5: *The peak according to the Table is 16 nm, please keep consistent to the Tables.*

R. It has been corrected.

R.1. Page 27406, line 26: How is the contribution of nucleation processes to the total number concentration calculated?

R. This is calculated by considering the percentage of time the Nucleation cluster occurred (5%, see Table 1) and the nucleation mode area in it (16%, see Table 2). This adds up to less than 2% of the particles, but we have to keep in mind that most nucleation processes affect particles below 15nm. Please see Dall'Osto et al. (2013a) for a detailed analysis where SMPS and CPC measurements are combined. The explanation has been added to the text.

R.1. Page 27407, line 4: “Hence, this section aims to investigate the effect of meteorology on N emitted in traffic hot spots during SAPUSS.” Rephrase this sentence.

R. It has been rephrased to: “Hence, this section aims to investigate the effect of meteorology on primary traffic emissions”.

R.1. Page 27407, line 10: What does the R-squared value reported here represent?

R. It represents the temporal correlation of cluster Traffic-2 at the RS_{site} with traffic counts at the RS reported in the Figure 2 of the SAPUSS overview (Dall'Osto et al., 2013b). We added this information to the text.

R.1. Page 27407, line 27: The rest of this paragraph is only weakly demonstrating some dependence on RH, after several restrictions. Additionally, there is too much is discussion about Figure S5 that if the authors believe is so important for interpreting the data should be incorporated in the manuscript.

R. We have reduced the text and argue that the correlation is weak.

R.1. Page 27407, line 8: R-squared values ought to be positive.

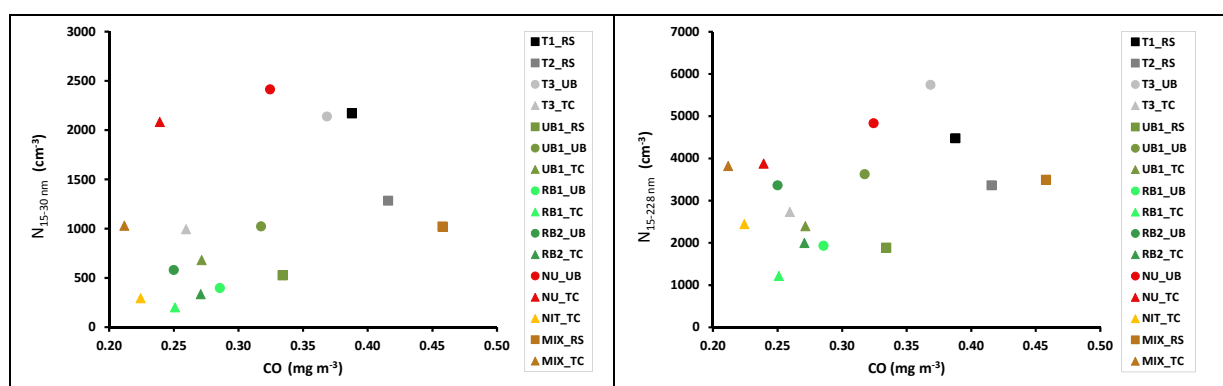
R. It was a mistake, the R-squared value was positive. Due to the text reduction suggested above, this sentence has been deleted from the text.

R.1. Page 27407, line 25 –line27: These sentences should be in the caption of the Figure.

R. This has been done as requested.

R.1. Page 27409, line 5: The same analysis would be interesting for CO concentration as well.

R. A similar conclusion to NO₂ and BC can be reached for CO, therefore we have mentioned it in the text but have not included the figures.



R.1. Page 27410, line 13: “This study shows that meteorology strongly affects the concentration of ultrafine particles of secondary origin.” This is not shown in the manuscript.

R. This sentence was deleted.

R.1. Page 27410, line 16: “This study also clearly shows that evaporation of traffic-related ultrafine aerosols occurs when the air mass move away from the traffic hot spot.” This is not clearly shown in the manuscript it is rather hypothesized.

R. Please refer to Dall’Osto et al. (2011) where a detailed study on traffic related particles were investigated during the REPARTEE project in London. Also, the summary of the study can be found in Harrison et al 2012 (REPARTEE overview summary paper), where the evaporation of traffic related particles is reported. The modes of cluster Traffic-1 moving to cluster Traffic-3 clearly shows in this study the shrinking of traffic related particles when moving away from the source. This last reference (Harrison et al., 2012) has been added to the text.

Technical Corrections

R.1. Page 27396, line 1: The percentage is 30%

R. It has been corrected.

R.1. Page 27409, line 16: Correct Figure 5f to 4f.

R. It has been corrected.

R.1. Page 27418, Table 4: It is not clear what is highlighted, explain in detail or correct(eg.WS of RB1)

R. We agree with the referee, there were some values mistakenly highlighted that have been corrected.

R.1. Page 27419, Figure 1: Change the scale in the middle panel so that the distributions become apparent. The size distributions displayed are beginning from 10 nm. Once again, what is the fitting and averaging tools you use? Why the distributions do not start from 15 nm?

R. The scale in the middle panel has been changed as requested. The size distributions were extrapolated by using the raw size distributions, depending on the size range of each site (section 2.2.1). In other words, we considered the size distributions 10-228 for the clustering methods for consistency across the sites. Then, we looked at the temporal trend of the clusters and compared them with the raw data at each site. Good agreement was found (indeed showing the clustering method well representing the raw size distributions), therefore the extrapolated size distributions are reported. We added explanations on it to the text.

R.1. Page 27420, Figure 2: The data presented here cover the 02:00-23:00 time frame and the other hours are neglected, fill in the rest of the hours. Furthermore, replace counts to frequency or fraction so that a relative contribution can be estimated.

R. It has been edited as requested and Figure 2 has been replaced.

R.1. Page 27422, Figure 4: In the print out this Figure is not clear, better resolution would be appreciated.

R. The resolution will be better in the final version.

Referee #2:

General Comments

R.2. *The paper fits well into the scope of the ACP journal. It analyzes data on aerosol number size distributions collected at four sites in Barcelona and its vicinity using SMPS spectrometers to show the aerosol dynamics within an urban area. By a k-means cluster analysis collected size distributions are sorted into 9 clusters in three categories: traffic, background and special cases. Average particle size distributions are shown for each cluster with their characteristic modes and their significance. Number concentrations corresponding to individual clusters are further correlated with concentrations of gaseous pollutants. Mutual relationships between the clusters and their relation to main meteorological parameters is studied as well. The methods used in the paper are sound and chosen adequately. The references relate the paper to other studies on similar subject. The scientific results are presented clearly, structured reasonably and written concisely.*

R. We thank a lot the comments and we celebrate that the referee thinks that the paper fits in ACP and that the presentation is reasonably acceptable.

Specific Comments

R.2. *There is one issue that is not touched in the paper and, in my opinion, needs to be answered: How the aerosol samples (analyzed by SMPS spectrometers) were treated concerning their relative humidity? It is indicated in chapter 2.2.1. that at the RB site the SMPS spectrometer was an EUSAAR IfT model, therefore it can be assumed that the RH inside the SMPS was kept under 40% to measure dry sample according to the EUSAAR standard. However, the other three SMPS systems deployed at the RS, UB and TC sites were combinations of different TSI DMAs and TSI CPCs. There is no more information on these systems in the paper, but I would assume that there must have been done some changes on these systems in order to incorporate aerosol driers into them to lower the RH below 40%. Otherwise, the size spectra measured at higher relative humidities might have been shifted towards larger sizes due to particles hygroscopic growth, so the spectra would not be directly comparable to the RB site. As can be seen in Figure S5, almost all samples were taken at ambient RH higher than 40%. I assume that the authors will be able to answer this question adequately. Failure to treat the RH of the samples adequately might have led to misinterpretation of the results.*

R. We are aware that a drier for each SMPS should have been used; however this was not possible during the SAPUSS campaign (Autumn 2010). The RB SMPS drier (EUSAAR Fitting) was first installed the 4th of November 2010, when the SAPUSS campaign had already finished (20th October 2010). This study aims to summarise different aerosol size distributions, which are grouped in 9 broad clusters. This is done for 4 different sites. This is clearly an overview of the atmospheric conditions; it does not mean we can quantify all sources and processes occurring at the 4 monitoring sites. Clearly many more clusters would be needed. In other words, we greatly simplify the aerosol size distributions in order to compare the monitoring sites. Looking at the percentages of the clusters (Table 1-4, Figure 1- 4) and the correlation with meteorology and atmospheric gaseous and particles measurements, we believe those 9 clusters are very robust.

R.2. *It follows from the modal analysis of the cluster-averaged aerosol size distributions (Fig.1, Fig S1) that the accumulation mode has been found in only one of nine clusters (Regional Background 1). I consider this result rather surprising. Is it because the number concentration of particles under the accumulation mode was so low that the “peak-fitting procedure” found only one or two major peaks (corresponding to nucleation and Aitken modes) and failed to find the peak connected to the accumulation mode? Could it be caused by the fact that the harmonized size spectra (2.2.1., line 18) ended at 228 nm and so the fitting procedure did not give enough weight to the rather flat accumulation mode that would otherwise continue further*

to larger sizes? I am asking because it is widely accepted in the aerosol literature that the accumulation mode is practically always present in the atmospheric aerosol.

R. This is due to a number of issues. First, the particle number size distribution is dominated by the nucleation and Aitken mode particles. Although the majority of the clusters are dominated by these two modes, the accumulation mode dominates the Regional Background 1 cluster, which represents 15% of the time. But this is not meaning that accumulation mode is low, especially at RB site. Surely the reviewer is right and part of the problem may be due also to the 228 nm size limit.

Technical corrections:

R.2. Abstract, line 18: the harmonized SMPS size range was 15-228 nm, so the last paragraph makes a rather general statement that is not directly supported by the SMPS data presented in the paper.

R. Yes, we agree, and we have edited the paragraph: “Within our measurement range of SMPS ($N_{15-228 \text{ nm}}$) and Condensation Particle Counters CPC ($N_{>5 \text{ nm}}$), we found that ultrafine particles within the range 5-15 nm in urban areas are the most dynamic, being a complex ensemble of primary evaporating traffic particles, traffic tailpipe new particle formation and non-traffic new particle formation.”

R.2. 1.Introduction, line 23: urban “agglomerations” instead of “agglomerates”

R. It has been corrected as suggested.

R.2. 2.2.1, page 27394, lines 10-15: it would be useful for the reader to add here information concerning how the samples were treated concerning their relative humidity.

R. We added explanation to the text, as requested: “Although the use of aerosol drier is advisable (Colbeck et al., 2014, Swietlicki et al., 2008) in future studies, unfortunately it was not possible during this campaign.”

R.2. 2.2.1., page 27395, line 2-3: the water-based TSI CPC might have been less sensitive to some freshly emitted particles, this model of CPC is more sensitive to aerosol composition than the butanol-based models. It would be helpful to the readers to explain how this might have influenced the results.

R. The issue of different CPC is discussed in the paper and in the overview (Dall’Osto et al., 2013b). The CPC’s were intercompared before and after the campaign, giving excellent overlap, with uncertainties around 5% both times. However, the water-based CPC 3785 (low-cut point at 5nm) gave slightly higher readings than the butanol-based CPC 3022A (low-cut point at 7nm). Previous studies (Biswas et al., 2005) performed a comparative analysis between the two CPC models in different environments and with different aerosol sources. Although for the smallest sizes the W-CPC measured slightly higher concentrations due to its lower cut-point, it recorded slightly lower concentrations for particles above 50 nm. However, they concluded that both instruments showed a similar response, always within the uncertainty of the manufacturer ($\pm 10\%$). For our study (a simplification of aerosol size distributions in 4 different sites) we only used 9 broad clusters, and for the scope of this study we believe the data can be compared.

We added to the text: “The CPC’s were intercompared before and after the campaign, giving excellent overlap, with uncertainties around 5% both times (Dall’Osto et al., 2013b). Biswas et al. (2005) intercompared both water-based and butanol-based instruments and concluded that they showed a similar response, always within the uncertainty of the manufacturer ($\pm 10\%$).”

R.2. 3.1., page 27397, line 26: In Table 3 and Fig S5 the North African air masses are further divided into East and West (NAF_E, NAF_W). The text here should be consistent with tables and figures.

R. Yes, the referee is right. It was a mistake that has been corrected.

R.2. 3.1.1.-3.1.3.: Notation of Figs 2, a-j is shifted in the whole section by one letter, e.g. on page 27398 line 13, Fig 2a should be Fig 2b. This shift continues all the way down to page 27401.

R. Yes, the referee is right. It was a mistake that has been corrected.

R.2. 3.1.2, page 27400, line 6: should be “15%” instead of “14%”

R. Yes, it has been corrected.

R.2. 3.1.3., page 27401, line 9: should probably be “Table 4” instead of “Table 1”.

R. Yes, it has been corrected.

R.2. 3.1.3., page 27402, line 9: formulation “the coarser mode” may mislead the reader who expects the coarse mode particles to be well above one micrometer in diameter.

R. Yes, the referee is right; we have changed it to “the larger size mode”.

R.2. 4.1, page 27403, lines 25-29: Why would nucleation mode particles evaporate and, at the same time, the Aitken mode particles grow by condensation? Should there not be a better explanation of the observed behaviour?

R. The nucleation mode peaks of clusters Traffic 1 and 2 located around 20-30 nm account mainly for organic carbon, while the second peak in the Aitken mode around 40-60 nm is representative of the elemental carbon fraction. The volatile nature of OC favours evaporation of VOC, thus reducing the particle size mode and concentration of the nucleation mode, while the EC fraction tends to grow by condensation and coagulation of VOCs. Therefore, when moving away from traffic sources, typical fresh traffic size distributions (Traffic-1 and Traffic-2) undergo atmospheric processes that lead to a different size distribution (Traffic-3), with a reduction of particle size in the nucleation mode by evaporation of VOC and a particle growth by condensation and coagulation of the Aitken mode, resulting in a size distribution like Traffic 3.

We added to the text: “This shows that fine OC mode aerosols (more volatile) tend to evaporate whereas the EC solid aerosols (more stable) do not (Dall’Osto et al., 2011; Harrison et al, 2012).”

R.2. 4.2., page 27406, line 4: Should not be there UB1 instead of NITclus? (see Fig 1)

R. This paragraph refers to Figure 3, where indeed clusters RB1, RB2 and NIT have the largest modal diameter. The last two sentences have been edited to clarify this: “The lowest particle number concentrations and the highest modal diameters are related to regional background conditions (RB_{clus_1} , RB_{clus_2} , NIT_{clus}). Finally, all these diverse clusters contribute directly into the urban background general aerosol particle spectra (UB_{clu_1}), which is indeed at the centre of Figure 3.”

R.2 In several Tables and Figures the information is not well readable in the printed version: namely in Table 4, Fig.2, Fig.4.

R. The resolution will be better in the final version.