General answer to all reviewers

We have noticed that some comments were common to all the reviewers and we would like to address them broadly to clarify some points before answering them in detail to each reviewer as required.

We have extended the climatic consideration from "Mediterranean climate urban environments" to "high insolation urban environments", thus shifting the main focus of the paper to the cities of Barcelona, Madrid and Brisbane. Given that the sampling site in Rome is located in a rural environment and the Los Angeles data set is limited in comparison to the others (3 months versus 1-2 years), these two cities have been used to complement the study but are no longer the main focus of the paper. Thus, the revised version concentrates on the 3 above-mentioned cities, for which long data sets (1-2 years) of particle number size distribution were available. The same methodology (*k*-Means clustering analysis) has been applied to all cities, allowing the direct comparison between sites in high insolation urban environments. The analysis of the data has enabled us to amalgamate a small number of very robust clusters that have been classified into different categories, being Traffic and Nucleation the most relevant ones. Traffic clusters dominated during rush hours and showed very high NO_x levels, as opposed to the Nucleation clusters, which occurred at midday under high temperature, solar radiation and ozone, and low NO_x levels. We specifically aim at studying and comparing the nucleation events in worldwide high insolation urban environments, focusing on their specific characteristics, such as their occurrence, duration and temporal evolution.

Reply to referee #1 on behalf of all co-authors

General Comments

The MS mainly deals with the evaluation of SMPS data sets for 5 measurement sites by k-means clustering analysis. The idea of the study is good, its goals are relevant, timely and of interest for the international scientific community in the field. Unfortunately, the work has not been performed on a scientific level that merits the high standard of the ACP, and it contains several confusions and mistakes.

Response: We thank the referee for believing that the idea of the study is timely and scientifically relevant, and we regret that he feels the manuscript does not meet ACP standards. We have worked a lot to prepare a completely revised manuscript and we believed that we took into account all the specific issues raised by the referee. Please see details below.

1. Selection of the measurement sites and corresponding time intervals is not justified. Brisbane does not belong to the Mediterranean climate zone as shown in Fig. 1, which is in contradiction with the title. (The source of Fig. 1 is not given and the type of the climate classification system is not mentioned.) Los Angeles can not be accepted as well since a 3-month long data set is only available for it, which A) does not cover one full year, and therefore the seasonality in the nucleation frequency (which is obvious in many areas) is disregarded, and B) it is also much shorter than for the other sites, thus 1 or 2 years. Furthermore, the measurements in Rome were *performed at a regional background site (p. 6), which is again in contrast with the title, and questions the representative character of the conclusions for urban areas.*

R: We agree that the title was not completely in accordance with the selection of the measurement sites and their characteristics. Therefore, the title has been changed to “Frequency of nucleation events in high insolation urban environments”. We modified completely the manuscript to focus mainly in the cities of Barcelona, Madrid and Brisbane, which are all located in urban environments with high insolation. Data from Rome and Los Angeles are used only to complement the results and give supportive examples that these regions may also undergo the same UFP processes than the core cities, but are not longer the main focus of the paper in accordance with the comments from the referee. Although the data for Los Angeles are scarce in quantity, the photochemically driven nucleation processes have been previously documented (Hudda et al., 2010) in the study area, being very intense during the warmer months. We believe it is important to show this phenomenon is occurring in such urban areas. Although Rome is considered a regional background site according to EMEP, it is regularly impacted by the pollution plumes from the city centre of Rome, and the detection of grown particles that nucleated downwind from that area and were advected to the sampling site has already been reported by Costabile et al. (2010). But, as suggested, we took out these sites from the core interpretations of the paper and are used only to exemplify processes.

Fig. 1 has been changed, its source acknowledged and the climatic classification system (Köppen) has been mentioned in the text.

2. It is generally and well accepted that frequency of the new particle formation event is determined on a daily basis, and that it represents the number of nucleation days with respect to all/relevant days on a certain time scale (week, month or year). The title of the paper is misleading not only because the concept of the frequency is completely different here, but - more importantly - since it can not be related to the nucleation event itself (see also comment 3). Instead, it expresses the time share of the particle growth process. At the same time, it is the end of the growth process that is difficult to determine in urban environments due to, for instance, substantial emissions, and therefore, the frequency concept suggested here is doubted.

R: The reviewer is right pointing out that frequency is generally attributed to the percentage of days on which nucleation events occur. Given that our measurements have an hourly resolution, we provide the frequency accordingly. There are several papers reporting the daily occurrence of nucleation events (Yoon et al., 2006 and 2007; Salma et al., 2014), hourly occurrence (Dall’Osto et al., 2011, 2012, 2013) or periods longer than 24 hours (O’Dowd et al., 2010). Moreover, in previous studies that have applied the k-Means clustering technique it is common to report the percentage of time (hours, usually) each cluster represents (see Dall’Osto et al., 2012; Sabaliauskas et al., 2013; Brines et al., 2014; Beddows et al., 2014; Salimi et al., 2014).

It is true that many processes and sources may affect urban areas, which might be difficult to separate. Therefore, simultaneous gaseous pollutants concentrations and meteorological parameters were recorded in order to attempt a realistic interpretation of the results. Moreover, the k-Means analysis has been reported to be a very strong statistical tool to apply on size distribution data, which highly simplifies its analysis. This technique has been compared to other statistical techniques and has been found to be the most adequate for such analysis (see Beddows et al., 2009; Salimi et al., 2014). It has been successfully applied to large data matrices containing large data sets and from different sites (Beddows et al., 2014). The method itself is quite robust in separating the most different clusters while keeping the cluster number to the minimum.

To account for the suggestions of the referee and complement our study, the percentage of nucleation days in each city has been calculated and added to the discussion. Moreover, the nucleation days were classified regarding the uninterrupted number of hours the Nucleation cluster prevailed at each of the main cities. The following table was included and discussed in the manuscript:

Table 4: Percentage of days with nucleation events at the main cities BCN, MAD and BNE, and the uninterrupted time prevalence of these events.

City	1 h or more	2 h or more	3 h or more	4 h or more
Barcelona	67%	54%	43%	28%
Madrid	69%	58%	41%	30%
Brisbane	67%	53%	37%	27%

3. The lower diameter measurement limits (between 10.2 and 17.5 nm) and the corresponding measurement diameter interval make the evaluation of the atmospheric nucleation events rather difficult in particular in cities since the most valuable diameter range, namely the interval below 10 nm is completely missing. As a consequence, the authors show a contour plot in Fig. 5 for Rome as a nucleation event although there is no indication of the nucleation mode (below 10-20 nm), and the elevated concentrations only appear above 20 nm, which is typical for emissions. This all questions if there was atmospheric nucleation at all that day. Such an unusual atmospheric event can not be classified or regarded as nucleation without firm and detailed explanations and evidence. Thus, the conclusions draw at a later stage are also not plausible. Let me also mention here that the heading of Fig. 5 "Daily average SMPS size distributions on a nucleation day" seems to be obscure similar to many other formulations (p. 2: collected size distributions, p. 6: data were sampled, title of section 2.2.1, etc.) in the text, which may indicate that the MS was not elaborated carefully and by all co-authors.

R: It is well accepted that nucleation clusters form at 1-3 nm, however very few research groups in the world have access to technologies required to measure those clusters. Many research papers have reported the growth of nucleated particles with instruments having a low size range of 10 nm. We accept that it might have not been clearly stated in the text that we were measuring grown nucleated particles, and we have amended it by adding this explanation to the text in the methodology.

We also added to the text that nucleation events were also evaluated visually by inspecting the trends of the SMPS size distributions (i.e., the "banana" or nucleation burst events). Furthermore – i.e. Figure 5 - shows the trends of NOx and the frequency of the nucleation cluster- to check whether the ultrafine plumes were of primary or secondary origin.

In general, NOx concentrations were 30-65% lower during nucleation events than usual (as stated in Fig 5 legend). Namely, in the case of Rome, it has been demonstrated that the air masses transported with the sea-breeze while passing over the city centre of Rome become progressively enriched in photochemical oxidants, and that under high pressure conditions the maximum photochemical production in the Tiber valley occurs between the city limits of Rome and the suburban areas located 15 km from the city centre (Ciccioli et al., 1999). Indeed, the dominant wind direction for the nucleation cluster is SW (morning sea breeze) therefore indicating the transport of nucleated particles downwind of Rome towards the sampling site. It must also be taken into account that this cluster occurs in the afternoon, and it is entirely plausible that the nucleated particles downwind of Rome have grown in size while being transported towards the sampling site by the sea-breeze. This concept is reported in great detail in Dall'Osto et al. (2013), where simultaneous measurements of a growing nucleation event is reported from the urban city centre of Barcelona, growing while transported outside the city, in the afternoon, with minimum amount of BC and NOx. Moreover, Costabile et al. (2010) found a PCA factor (PC2) attributed to an aged nucleation mode with a size peak comprehended between 20.2-33.4 nm, which is in agreement with the size distribution of the Rome Nucleation cluster (23±1 nm). In any case, Rome and Los Angeles data sets are no longer the main focus of the manuscript and the text was modified accordingly.

The title of section 2.2.1 has been changed to “Particle number size distributions”.

The heading of Figure 5 has been changed to “Mean SMPS size distributions on a nucleation day at each selected city...”.

We improved the English usage in the revised version that has been validated again by all authors.

4. It is not described at all how the number of representative clusters between 7 and 15 was reduced “after a careful consideration” (p. 8) to 4-7, which could be a critical issue, and lacks objectivity in its present form.

R: The number of clusters was conservatively chosen using the Dunn Index and the Silhouette Width. The larger the Dunn Index and Silhouette Width, the more compact, well separated and similar were the elements within each cluster (Beddows et al., 2009). Preference was given to a solution with a higher cluster number to reduce the likelihood that any one of the clusters grouped together spectra reflects more than one source. Although we reduce the possibility of losing information by 'over-clustering', it is likely that when comparing the average size distributions - together with the corresponding gaseous pollutants, meteorological parameters, and various temporal trends (daily, weekday-weekend, monthly) - that more than one size distribution may (or even may not) originate from a similar process/source. More often than not, when considering the average size distributions and auxiliary measurements from over-clustered data (e.g. similarly low NO concentrations among the clusters, similar daily trends…), one or more clusters are combined together thus reducing the number of clusters in the final solution. This technique has been applied in several works (Beddows et al., 2009; Dall’Osto et al., 2012; Brines et al., 2014). An explanatory text has been added in the supporting information to clarify this issue.

5. It is unusual to use “traffic-related nucleation mode” (e.g. on p. 9) because the particles which are formed within the source, plume or exhaust are considered as primary particles contained in the Aitken mode in contrast to the nucleated particles contained in the nucleation mode. The present reviewer admits that this can be somewhat more complex (see Robinson et al., Science 315, 1259-1262, 2007) but the usage of such expression without further specific explanations is not tolerable.

R: Vehicular exhausts gases emitted into the atmosphere are cooled and diluted after leaving the tailpipe, leading either to nucleation and new particle formation (in the large nucleation and early Aitken mode, 10-30 nm) or condensation onto pre-existing particles (Aitken and accumulation mode) according to Charron and Harrison (2003). The volatile components of the particles can later evaporate and condensate onto other existent particles, according to Robinson et al. (2007). Therefore the study of the processes affecting traffic particles is rather complex and beyond the main objectives of the paper. But as suggested we clarified and changed the nomenclature to avoid the size mode and secondary/origin process links for the exhaust emissions.

6. Fig. 2 shows particle number size distributions that resulted from k-means clustering. After a detailed examination of many curves, the readers can wonder if resolving the distributions of atmospheric aerosol particles into two modes is indeed realistic, or in other words, whether the clusters T1, T2 and T3 containing 2 modes each at 1)20-40 nm and 70-130 nm, 2) 20-40 nm and 60-90 nm, and 3) 10-20 nm and 50-80 nm are indeed different.

R: The size modes for each curve at each site were obtained by the log-normal fitting method. Moreover the complementary gaseous pollutants concentrations averages, meteorological parameters and temporal trends pointed to some differences that did not enable to merge the traffic clusters. Namely, traffic T1 was related to fresh traffic emissions, thus containing high concentrations of smaller particles in a range of 20-30 nm. T2, on the other hand, was observed in the evening and night, reflecting the possible traffic particle growth due to condensation of volatile gaseous compounds on existing particles and coagulation processes. Regarding T3, the reduction in size of the 20-40 nm of the T1 and T2 clusters may indicate the occurrence of some evaporation processes, as it is detected during daytime. The biggest difference in the spectra could be observed between T3 and the other Traffic clusters. The sources and processes reflected in the 3 Traffic clusters are in accordance with the complex scenario described by Robinson et al. (2007) and merging them into one cluster would lead to a loss of useful information. This same classification and a detailed analysis on the link between T1-3 can be found in Brines et al. (2014). Also, different traffic clusters had been previously reported in Dall'Osto et al. (2011) in a different environment (London, UK).

7. In relation to comment 6, a sensitivity analysis or arguments should have been added on the uncertainty of some results. Without these, it can be questioned whether the frequencies of 6% (section 3.1.3) or 7% (section 3.1.4) are significant or just within the uncertainly limits.

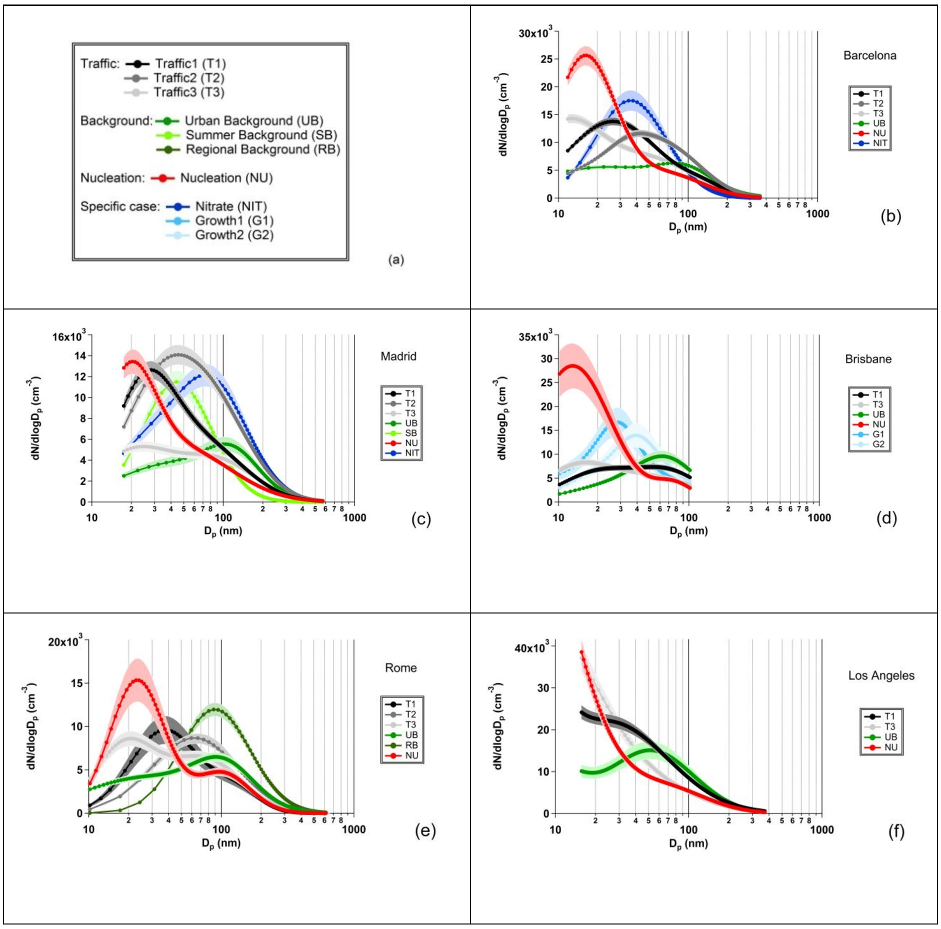
R: The nucleation clusters are unique, showing a very distinctive particle size distribution with very high particle concentration in the nucleation mode, high solar radiation, high ozone concentrations, low black carbon/NOx concentrations, etc. Therefore we believe the nucleation clusters resulting from the k-Means are accurate. The Nitrate cluster reported in Barcelona is site-specific, and although it might contain other particle sources, its temporal and seasonal trends are quite revealing (higher occurrence at night during cold months). Moreover, it has already been reported by Brines et al. (2014) for the city of Barcelona.

We have calculated the 99.99% uncertainty for each cluster size distribution at each city using the confidence limits μ:

$$\mu = mean\ (x) \pm t\frac{\sigma}{\sqrt{n}}$$

where x are the size bin values dN/dlogD_p, n is the number of values used in the average, σ is the standard deviation, t is the Student t-value. We approximated the degrees of freedom to ∞, due to the high number of hours contributing to each cluster - in the range of hundreds to thousands. We considered 99.9% of confidence level, obtaining a t-value of 3.291 according to http://www.webassign.net/harrischem/4-02tab.gif. An explanatory text has been added to the manuscript and a more detailed explanation can be found in the supporting information to address this issue.

The uncertainty bands plotted for each cluster show that there is a 99.99% chance than any of the elements within each cluster are miss-classified by the analysis. As can be observed in the modified figures below, the highest uncertainty can be found in the size peaks, although no spectra overlapping is detected at any of the sites. Therefore, the k-Means clustering method is proven to be very robust.



Several comments listed above represent excluding criteria or arguments for rejection, and it is thought that the MS needs such an extensive improvement which can only be realised within the frame of a new submission.

R: As the referee will see, the revised version has been completely modified to account for all suggestions and comments raised. We have put a considerable effort into this revision and we believe that now the revised version has improved a lot the quality of the presentation of the results.

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Reply to referee #2 on behalf of all co-authors

General Comments

The paper presents results from 5 different measurement sites: 3 in the Mediterranean, one in Australia and one at west coast of the US. Analysis of number size distributions using statistical methods might be a valuable tool for such data sets. However, the present study needs improvement in data analysis and interpretation.

Response: We are thankful to the referee for the comments and we hope that the deep changes and improvements implemented in the manuscript reach his/her expectations.

Comments in detail

The five measurement sites are supposed to have similar climatic conditions but the sources for precursor gases and also aerosol particles might be very different. The 3 months of measurements from Los Angeles do not really fit into the study and should be excluded, because such a short period is not representative at all. All other sites have at least 1 year of measurements. One could also discuss if Brisbane fits into the study, but maybe it is a chance to find some differences.

R: As explained in the answer to reviewer #1, the manuscript now focuses on the cities of Barcelona, Madrid and Brisbane (three cities with high insolation), as all sampling sites are located within the urban environment and 1-2 years of aerosol size distribution data were available at all sites. Thus, in the revised version Rome and Los Angeles data are only used to complement the study but are no longer the core data evaluated in the paper. Therefore, the title and focus of the paper has softened to new particle formation events in urban environments with high solar radiation. Nonetheless, a new table has been introduced showing the meteorological annual characteristics of all sites and PN from 17.5-100 nm (common range for all 5 sites) during the study periods.

Table 1: Average annual meteorological parameters for each site during the respective study periods. Due to the reduced data availability in LA, values in brackets represent annual values provided by NOAA or NASA.

City	T (ºC)	RH (%)	Rain (mm)	Solar radiation (Wm^{-2})	$PN_{17.5-100nm}$ (cm^{-3})
Barcelona	18±6	68±16	432	190±270	7500±5000
Madrid	15±7	66±23	438	182±265	7000±8000
Brisbane	20±5	72±20	1072*	240±337	6000±7000
Rome	19±7	59±17	$732^{\#}$	203±274	5000±3000
Los Angeles	19±6 ($19^{\$}$)	58±20 ($71^{\$}$)	126 ($452^{\$}$)	(225^{+})	12000±7000

* Australian Government Bureau of Meteorology

http://www.weatherbase.com/weather/weatherall.php3?s=124261&refer=&units=metric

$^{\$}$ National Oceanic and Atmospheric Administration (NOAA)

$^{+}$ National Aeronautics and Space Administration (NASA)

Furthermore, the following text has been added to the manuscript in the Methodology section to support the selection of the cities/data for our focus and to take into account your comments on additional patterns governing UFP:

“Although the selected cities are located in similar climatic environments, some differences regarding meteorological conditions were encountered (see Table1). All cities show mild annual temperatures, ranging from 15ºC in Madrid (due to its inland location) to 20ºC in Brisbane (due to its latitude, closer to the equator, see Figure 1). Relative humidity varies by 10% across the cities, showing highest values in Brisbane (72%). This is probably related to the higher precipitation rate registered in this city (1072 mm), two times higher than in BCN, MAD or LA (430-450mm). As expected, the highest average annual values of solar radiation are recorded in Brisbane and the lowest in Madrid (240±337 Wm^{-2} and 182±265 Wm^{-2}, respectively). UFP concentrations (common size range 17.5-100 nm) showed lowest levels in Rome (due to the location of the sampling site, 5000±3000 cm^{-3}), followed by Brisbane, Madrid and Barcelona (6000±7000 cm^{-3}, 7000±8000 cm^{-3} and 7500±5000 cm^{-3}, respectively). The highest concentrations corresponded to the city of LA (12000±7000 cm^{-3}), probably due to the proximity to the freeway and the limited sampling time (3 months).

In addition to meteorological features, emission sources also have an impact on UFP in urban environments, especially traffic related pollutants. The vehicle fleet composition is not homogeneous among the sampling sites, as a tendency towards dieselization has been experienced in some European countries over the last years, especially in Spain (Amato et al., 2009), where 55% of vehicles are diesel-powered versus 44% gasoline (Dirección General de Tráfico, 2015). In Italy 37% of the vehicles used diesel fuel and 62% used gasoline in 2007 (Istituto Nazionali di Statistica, 2009). On the other hand, in the USA or Australia the diesel share represents only around 20% (Gentner et al., 2012; Australian Bureau of Statistics, 2014). Diesel vehicle engines are known to emit much higher PN than gasoline ones (Harris and Maricq, 2001), which might imply a higher concentration of primary UFP in European countries in comparison to the USA and Australia. Another relevant difference between the cities relates to their urban structure. While both Brisbane and Los Angeles are extensively suburbanised cities with relatively low population densities, favouring dilution and diffusion of pollutants, southern European cities are dense urban agglomerates that favour the trapping and accumulation of pollutants. The lower concentrations of UFP in Brisbane in comparison with European cities are therefore likely due to lower primary diesel emissions and higher precipitation rates, coupled with higher diffusion and dilution of pollutants due to the urban geography of the city. In the case of Madrid and Barcelona, the higher proportion of diesel vehicles together with the high urban density leads to an increase of UFP concentrations. In the case of Los Angeles, the high readings are probably due to both the proximity to the traffic source and the reduced sampling period (3 months). Given these differences between the cities, we nevertheless view the climatic similarities to be strong enough to consider the urban background environments in which the data have been sampled to be broadly comparable."

My major criticism is the quantification of traffic related particles and new particle formation. I think it is difficult to distinguish between these groups, because also from traffic-emitted gases new particle formation takes place. These particles are typically measured at roadsites with mean diameters of 10 - 20 nm. This is the same size range as new particle formation in the present study. There are several studies published about measurements behind the car and at the roadsite. What does new particle formation (NPF) mean here? Does it include only NPF from natural sources or also that from traffic-related gases? The first one is probably not possible to investigate in cities like Barcelona and Madrid. Thus, new particle formation in big cities is always connected to traffic emissions.

R: We do not wholly agree with the referee. Particle nucleation occurs within traffic emissions, leading to nucleation mode particles in the size ranges from 10-20 nm immediately after emission. These particles form within metres of the tailpipe and are regarded by convention as primary particles. NPF can occur due to photochemical nucleation when traffic emissions are at their lowest. These NPF are regarded as secondary particles and occur when primary traffic emissions are low - usually at midday-, and can be distinguished from primary emissions. A low condensation sink coupled with high solar radiation, low relative humidity, relatively high SO_2 levels and high wind speed favour photonucleation processes. Reche et al. (2011) showed that in southern European urban environments (higher solar radiation than in the northern ones) NPF occurred at midday when black carbon levels were low and SO_2 levels were relatively high. Therefore, these newly formed particles were attributed to photochemical nucleation events, as under the same conditions (low black carbon and high SO_2 levels) NPF did not usually occur at midday in northern European cities, given the lack of intense solar radiation.

Traffic emissions follow a different daily trend, usually dominating during traffic rush hours. In our study, cluster T1 reflects fresh traffic particles and include primary emitted particles as well as those formed by nucleation processes near the vehicle exhaust pipe. Therefore, to clarify this point we have added "photochemical" when referring to "nucleated particles" or "nucleation events", as the particles resulting from photochemically driven nucleation processes are the main focus of the paper.

Case studies, Figure 5: Figure c) Rome: A burst of particles around 30 nm in size occurs in the afternoon. How do the authors conclude that this is NPF? Where have these particles been formed and when? Such a figure does not fit into the general understanding of new particle formation, because it starts at small sizes and includes also particle growth. If particles appear at larger sizes, they might have been formed somewhere else, but this has to be discussed!

R: The referee is right that the particles burst registered at the Rome site reflect particles growth rather than NPF. The Nucleation cluster size distribution shows a size peak at 23±1 nm (highest PN of all Rome clusters), occurring shortly after midday. This cluster is characterised by the highest solar radiation and temperature, high wind speed with a predominant SW origin (typical of sea breeze), low NO_x levels and the highest SO_2 and O_3 levels of all clusters. Similar characteristics were shared with the Nucleation clusters of the other cities. Moreover, previous studies (Costabile et al., 2010) found that the arrival of an aged nucleation mode particle burst after midday (20-33 nm size, PCA factor 2) coincided with a quick decrease of Aitken and accumulation mode particles as well as HONO levels, and high ozone levels. Ciccioli et al. (1999) had previously reported that the sea breeze air becomes progressively enriched in photochemically induced pollutants while crossing over the city centre of Rome and its suburban area and later reaching the sampling site in 1-2 h. Therefore, in addition to the unique characteristics of our Nucleation cluster, previous studies in the same area confirm that the aged nucleation mode particles detected at the Rome sampling site are photochemically induced nucleated particles downwind of Rome that have been transported to the sampling site by the sea breeze. Also in the western Mediterranean basin Dall'Osto et al. (2013) reported the detection of a particle burst in a regional area downwind of the city of Barcelona several hours after a nucleation event has occurred in the city. Those particles had experienced growth while being transported by the sea breeze to the areas downwind of the city. The following explanatory text has been added to the new results section 3.3 and to the discussion section, respectively:

"Indeed, previous studies have showed that an aged nucleation mode of particles in the size range 20-33nm is related to photochemically nucleated particles downwind of Rome growing in size while being transported to the sampling site (Costabile et al., 2010)."

"Indeed, previous studies reported that the sea breeze regime favoured the transport of photochemically transformed pollutants such as nucleated particles from the urban and suburban area downwind of Rome to the sampling site (Ciccioli et al., 1999; Costabile et al., 2010). This phenomenon has also been reported for the city of Barcelona by Dall'Osto et al. (2013), where several hours after the occurrence of a nucleation event originating in the city, a particle burst of 20-40 nm in size was detected at a regional site located 50 km downwind of the urban area, evidencing the growth of the nucleated particles while being transported away by the sea breeze."

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Reply to referee #3 on behalf of all co-authors

General Comments

This manuscript focuses on the analysis of SMPS data collected in five measurement sites (4 urban and 1 rural) during different measurement campaigns separately presented in already published works. Particle number size distributions were categorized in four different classes using the k-mean clustering analysis. The authors conclude that nucleation events accounted on average for 18 % of the observations. Even if the idea of aggregating SMPS data from different cities with the aim of statistically analyse nucleation events is interesting, the approach followed by the authors does not appear adequate to draw the strong conclusions presented in the manuscript. Recognizing the effort in answering to Referee #1 comments, the following specific issues still have to be properly addressed before the manuscript can be re-evaluated for publication in ACP.

Response: We thank the referee for his comments. We modified deeply the original submission and we believe now that we have taken into account most of the requirements highlighted by this referee. Please see details below.

1. The cities taken in consideration in the manuscript are not uniform in terms of climate, solar irradiation, humidity, aerosol (and aerosol precursors) concentration, aerosol sources and formation mechanisms. Differences of these parameters and mechanisms, their impact on NPF events (and conclusions) should be discussed for each location.

R: As explained in the answer to reviewer #1, the manuscript now focuses on the cities of Barcelona, Madrid and Brisbane (three cities with high insolation), as all sampling sites are located within the urban environment and 1-2 years of aerosol size distribution data were available at all sites. Thus, in the revised version Rome and Los Angeles data are only used to complement the study but are no longer the core data evaluated in the paper. Therefore, the title and focus of the paper has softened to new particle formation events in urban environments with high solar radiation. Nonetheless, a new table has been introduced showing the meteorological annual characteristics of all sites and PN from 17.5-100 nm (common range for all 5 sites) during the study periods.

Table 1: Average annual meteorological parameters for each site during the respective study periods. Due to the reduced data availability in LA, values in brackets represent annual values provided by NOAA or NASA.

City	T (ºC)	RH (%)	Rain (mm)	Solar radiation (Wm^{-2})	PN$_{17.5\text{-}100nm}$ (cm^{-3})
Barcelona	18±6	68±16	432	190±270	7500±5000
Madrid	15±7	66±23	438	182±265	7000±8000
Brisbane	20±5	72±20	1072*	240±337	6000±7000
Rome	19±7	59±17	732[#]	203±274	5000±3000
Los Angeles	19±6 (19[$])	58±20 (71[$])	126 (452[$])	(225[+])	12000±7000

* Australian Government Bureau of Meteorology

[#] http://www.weatherbase.com/weather/weatherall.php3?s=124261&refer=&units=metric

[$] National Oceanic and Atmospheric Administration (NOAA)

[+] National Aeronautics and Space Administration (NASA)

Furthermore, the following text has been added to the manuscript in the Methodology section to support the selection of the cities/data for our focus and to take into account your comments on additional patterns governing UFP:

“Although the selected cities are located in similar climatic environments, some differences regarding meteorological conditions were encountered (see Table1). All cities show mild annual temperatures, ranging from 15ºC in Madrid (due to its inland location) to 20ºC in Brisbane (due to its latitude, closer to the equator, see Figure 1). Relative humidity varies by 10% across the cities, showing highest values in Brisbane (72%). This is probably related to the higher precipitation rate registered in this city (1072 mm), two times higher than in BCN, MAD or LA (430-450mm). As expected, the highest average annual values of solar radiation are recorded in Brisbane and the lowest in Madrid (240±337 Wm^{-2} and 182±265 Wm^{-2}, respectively). UFP concentrations (common size range 17.5-100 nm) showed lowest levels in Rome (due to the location of the sampling site, 5000±3000 cm^{-3}), followed by Brisbane, Madrid and Barcelona (6000±7000 cm^{-3}, 7000±8000 cm^{-3} and 7500±5000 cm^{-3}, respectively). The highest concentrations corresponded to the city of LA (12000±7000 cm^{-3}), probably due to the proximity to the freeway and the limited sampling time (3 months).

In addition to meteorological features, emission sources also have an impact on UFP in urban environments, especially traffic related pollutants. The vehicle fleet composition is not homogeneous among the sampling sites, as a tendency towards dieselization has been experienced in some European countries over the last years, especially in Spain (Amato et al., 2009), where 55% of vehicles are diesel-powered versus 44% gasoline (Dirección General de Tráfico, 2015). In Italy 37% of the vehicles used diesel fuel and 62% used gasoline in 2007 (Istituto Nazionali di Statistica, 2009). On the other hand, in the USA or Australia the diesel share represents only around 20% (Gentner et al., 2012; Australian Bureau of Statistics, 2014). Diesel vehicle engines are known to emit much higher PN than gasoline ones (Harris and Maricq, 2001), which might imply a higher concentration of primary UFP in European countries in comparison to the USA and Australia. Another relevant difference between the cities relates to their urban structure. While both Brisbane and Los Angeles are extensively suburbanised cities with relatively low population densities, favouring dilution and diffusion of pollutants, southern European cities are dense urban agglomerates that favour the trapping and accumulation of pollutants. The lower concentrations of UFP in Brisbane in comparison with European cities are therefore likely due to lower primary diesel emissions and higher precipitation rates, coupled with higher diffusion and dilution of pollutants due to the urban geography of the city. In the case of Madrid and Barcelona, the higher proportion of diesel vehicles together with the high urban density leads to an increase of UFP concentrations. In the case of Los Angeles, the high readings are probably due to both the proximity to the traffic source and the reduced sampling period (3 months). Given these differences between the cities, we nevertheless view the climatic similarities to be strong enough to consider the urban background environments in which the data have been sampled to be broadly comparable."

2. Given the limited number and the different climatic characteristics of the cities analysed, the stated aim of "obtaining general conclusions on nucleation events in urban Mediterranean climate environments" results too ambitious and should be soften. For the same reason also the sentence at page 26478 lines 17-20 should be revised.

R: Due to the change of focus required by all reviewers, we have changed "urban Mediterranean climate environments" for "high insolation urban environments" and revised the manuscript accordingly.

3. The choice of the time resolution of SMPS data have to be better discussed and justified. One-hour resolution could be poor to spot nucleation events, and certainly an isolated single hour of nucleation-like size distribution is not indicative of a NPF event.

R: Due to the low cut-size range of the SMPS instruments (10-17.5nm), we are effectively recording the growth of already nucleated particles. Indeed, to spot the start time of nucleation events different instrumentation and time resolution should be used. However, we aim at obtaining a general picture of the dominant processes and sources affecting urban environments and our experience and that of similar papers (see Beddows et al., 2009, Dall'Osto et al., 2011 and 2012) shows that one hour is enough to obtain the separation of clusters. Overall, considering all 5 data sets over 30000 hours of size distributions measurements were computed. The increase in the computational costs and complexity that a higher time resolution would require were not considered appropriate for the scope of this paper.

4. Following the discussion at point 3, the authors should better explain the meaning of the proposed definition of frequency of nucleation events. As highlighted by Referee #1, since normally a single nucleation event occurs per day, the frequency of NPF events is generally defined as the ratio between the days showing a NPF event and the total number of days of measurement. In new Table 4: Defining "days with nucleation events" the ones with a single one hour long SMPS spectrum results in misleading figures, at least the first column of new Table 4 should be removed.

R: Our objective by defining the nucleation events as the percentage of time these particles dominate the aerosol spectra is to better quantify the impact of these events upon the overall sources of ultrafine particles in urban environments.

We aim to characterise the different ultrafine aerosol sources affecting urban environments, for which the classical "percentage of nucleation days" does not give any information. In fact, on a nucleation day, traffic sources would most probably also be a relevant particle source. Therefore the contribution of the different sources to UFP can be assessed by the time prevalence of each source.

By applying the *k*-Means clustering to reduce the complexity of the spectra and comparing with auxiliary parameters, the dominant source for each cluster can be determined. This enables us to identify the most common sources and estimate the relevance of each one. Applying this method to 5 worldwide urban environments showing similar climatic conditions, a comparison can be made. The following text has been added to the introduction section of the manuscript to clarify this issue:

"The identification of the main pollution sources contributing to ultrafine particles affecting urban environments enables quantitative estimation of the temporal prevalence of each source."

As requested, the first column of Table 4 (currently Table 5) has been removed from the manuscript.

5. Page 26478, line 12: The variability of PN concentration (9970 +- 100 cm-3) seems too small and should be cross checked.

R: Due to the changes applied to the manuscript, the average size distributions have been changed to consider only the main cities. Therefore the new value is: 12000±8000 cm^{-3}.

6. Page 26479, lines 7-11: The diversification of the two types of NPF events derive solely from another work, is not relevant for the discussion, and hence should be removed or better discussed.

R: What we want to stress is that even though photochemically nucleated particles usually grow over 3-4 hours reaching 30-40 nm in size, in some urban environments like Brisbane, banana-like events are observed more often than in the rest of the cities. These events are characterised by starting earlier than the urban nucleation type, and that enables their identification. The existence of these two types has already been reported by Dall'Osto et al. (2013). In this revised version we use their conclusions to interpret the duration of the growth stage according to the starting point of NPF, which is delayed in many cases by the condensation sink. We explain that the other paper defined the two types of NPF, and that we only discuss our data according to the two scenarios.

7. Page 26480, lines 5-8: The anthropogenic origin of the nucleation events is a speculation not supported by evidence. A single measurement site cannot provide information about where the NPF event initiated. The sentence is a conclusion of another work, is not strictly relevant for the discussion and hence should be removed or better justified and discussed.

R: We modified the text stating that "The urban nucleation events described in this paper presumably have an anthropogenic origin, or at least be influenced by anthropogenic precursors …" and we refer to the study where this is supported, instead of affirming that our results point to urban nucleation having an anthropogenic origin.

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Frequency of new particle formation events in high insolation urban environments

Eliminado: the urban Mediterranean climate

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Abstract

Road traffic emissions are often considered the main source of ultrafine particles (UFP, diameter smaller than 100 nm) in urban environments. However, recent studies worldwide have shown that, - in high insolation urban regions at least, - new particle formation events can also contribute to UFP. In order to quantify such events we systematically studied three cities located in predominantly sunny environments: Barcelona, Madrid and Brisbane. Three long term datasets (1-2 years) of fine and ultrafine particle number size distributions (measured by SMPS, Scanning Mobility Particle Sizer) were analysed. By applying *k*-Means clustering analysis, we categorized the collected aerosol size distributions in four main classes: "Traffic" (prevailing 44-63% of the time), "Background Pollution" (13-22%), "Nucleation" (14-19%) and "Specific case" (7-20%) the latter being site specific. Measurements from Rome and Los Angeles were also included to complement the study. The daily variation of the average UFP concentrations for a typical nucleation day at each site revealed a similar pattern for all cities, with three distinct particle bursts. A morning and an evening spike reflected traffic rush hours, whereas a third one at midday showed nucleation events. The photochemically nucleated particles burst lasted 1-4 hours, reaching sizes of 30-40 nm. On average, the occurrence of particle size spectra dominated by nucleation events was 16% of the time, showing the importance of this process as a source of UFP in urban environments exposed to high solar radiation. Furthermore, in a number of the studied cities, particle number concentration averaged daily profiles for the whole study periods clearly showed the same three particle bursts. This reveals nucleation events as a relevant contributor to the average daily urban exposure to UFP in high insolation urban environments. On average, nucleation events lasting for 2 hours or more occurred on 55% of the days, this extending to >4hrs in 28% of

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the days those, demonstrating that atmospheric conditions in urban environments are not favourable to the growth of photochemically nucleated particles.

1 Introduction

Ultrafine particles are ubiquitous in urban environments (Kumar et al., 2014). Due to their high number concentration and negligible mass, they have a great potential for lung deposition and are associated with respiratory and cardiovascular diseases (Atkinson et al., 2010; Oberdorster et al., 2005). Ultrafine particles can have a primary or a secondary origin. Primary particles are emitted during the dilution and cooling of road vehicle exhaust (Charron and Harrison, 2003; Kittelson et al., 2006) or as carbonaceous soot agglomerates formed by fuel combustion (Kittelson, 1998; Shi et al., 2000). Other combustion sources such as waste incinerators can also contribute to the UFP loading in urban environments (Buonanno and Morawska 2014). Secondary particles are formed through nucleation processes of gaseous precursors such as SO_2 and NH_3 in neutral or ion induced processes (Kulmala et al., 2004 and references therein).

It has been often assumed that photonucleation events only occur in background and regional environments such as clean coastal (O'Dowd et al., 2010), forest areas (Boy and Kulmala, 2002), semi-clean savannah (Vakkari et al., 2011), high altitude locations (Sellegri et al., 2010) and regional background sites (Wiedensholer et al., 2002). This is usually attributed to the fact that such environments have a low condensation sink (CS), thus facilitating nucleation. By contrast, urban environments are often characterised by high CS, so that a lower frequency of nucleation events is expected. Nevertheless, there are studies showing that these events in fact can be detected in urban areas, as initially demonstrated in Atlanta, USA (Woo et al., 2001), Birmingham, UK (Alam et al., 2003) and Pittsburg, USA (Stanier et al., 2004), and subsequently in many cities worldwide (Pey et

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High insolation and wind speed, low relative humidity, available SO_2 and low pre-existing particle surface area are common features that enhance new particle formation events (Kulmala and Kerminen, 2008), characterised by a great increase in particle number concentrations (PN) in the nucleation mode and subsequent particle growth, if conditions are favourable. Within Europe, nucleation events in many urban areas were not very often detected (Alam et al., 2003; Wegner et al., 2012; von Bismarck-Osten et al., 2013). However, Reche et al. (2011) showed that a different behaviour was observed in southern European cities, where new particle formation processes at midday did occur with higher frequency than in northern European cities. The main cause for this difference is suggested to be the higher intensity of solar radiation in the meridional European areas, and/or possible site specific chemical precursors.

The objective of this study is to categorise sources of UFP in urban environments situated in temperate regions affected by high solar radiation levels. Specifically, we aim to assess the frequency and influence of nucleation events on UFP levels and variability, as well as the atmospheric conditions facilitating such events. Although a number of studies have addressed this issue, we aim at an inclusive study that will lead to obtaining general conclusions on nucleation events in high insolation urban environments. Our main database is taken from two cities in Southern Europe (Barcelona and Madrid) and one in Eastern Australia (Brisbane). To complement the study, 2 more data sets from high insolation areas (also located in temperate climatic areas) are analysed; 2 years of data from a regional background site regularly impacted by the Rome (Italy) pollution plume and 3 months of data from an urban background site in Los Angeles (USA).

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Size-resolved particle number concentration measurements using a Scanning Mobility Particle Sizer, (SMPS, see Table S2 for details) were performed in each of the five cities. The complexity of the data was further reduced by applying *k*-Means clustering analysis (Beddows at al., 2009; Dall'Osto et al., 2011, 2012; Sabaliauskas et al., 2013; Brines et al., 2014; Salimi et al., 2014). This clustering technique classifies aerosol size spectra into a reduced number of categories or clusters that can be characterised considering their size peaks, temporal trends and meteorological and gaseous pollutants average values (Beddows et al., 2009). The identification of the main pollution sources contributing to ultrafine particles affecting urban environments enables quantitative estimation of the temporal prevalence of each source.

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2 Methodology

2.1 Site locations

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Four of the selected cities (Barcelona, Madrid, Rome and Los Angeles) are located in Mediterranean climatic regions, according to the Köppen climate classification (Figure 1). The Mediterranean climate is categorised as *dry-summer subtropical* (type Csa/b) due to its mild winters and warm summers with scarce rainfall. It is characterised by annual average temperatures of 12-18°C, with dominant clear sky conditions (annual global irradiance intensity of 180-190 Wm^{-2}). Precipitation is concentrated in autumn and spring and is very scarce during summer; its annual average is about 600 mm. Although it prevails in the coastal Mediterranean Sea Basin areas, it is also present in other parts of the world, such as south-western USA, the west and southern Australia coast, south-western South Africa and central Chile (see Figure 1). Three cities in the western Mediterranean Basin were selected for this study: Barcelona, Madrid and Rome. For the American continent the city of Los Angeles was chosen, (it is also located in a

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Mediterranean climate region). Finally, the city of Brisbane (Australia) was also included. Its climate is categorised as *humid subtropical* (type Cfa) due to the higher mean annual rainfall (1150 mm versus 600 mm for the Mediterranean climate), although otherwise presents many climatological similarities to the Mediterranean regions with mild winters and warm summers with prevalent sunny days (average annual global irradiance of 208 Wm^{-2}). A detailed description of the five selected cities is given below:

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1) Barcelona (BCN), Spain: located on the north-western Mediterranean basin it has 1.7 million inhabitants although the metropolitan area exceeds 4 million. Road traffic is the major emission source, although industrial, domestic, shipping emissions and occasional Saharan dust outbreaks also contribute to increase ambient PM levels. The SMPS sampling site (Palau Reial) is classified as urban background and is located close (350 m) to a major highway (Diagonal Avenue: 90 000 vehicles per working day), which is primarily used by commuters (see Table S1). Previous work in the study area has demonstrated that 65-69% of ultrafine particles are emitted by traffic and that photonucleation events contribute remarkably to the annual average total PN (Pey et al., 2008, 2009; Dall'Osto et al., 2012).

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2) Madrid (MAD), Spain: located in the centre of the Iberian Peninsula, it features 3.3 million inhabitants although the metropolitan area accounts for more than 6 million. Its air pollution plume is fed mainly by traffic emissions. The SMPS sampling site is located at the CIEMAT facilities, NW of the city centre and considered as a suburban background area (see Table S1). Previous work in the study area (Gómez-Moreno et al., 2011) analysed the influence of seasonality on two years of SMPS data. They found that nucleation mode particles showed high PN at midday, especially during spring and summer due to new particle formation.

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3) Brisbane (BNE), Australia: located on the eastern Australian coast, it has two million inhabitants although the metropolitan area accounts for 3 million. Traffic exhaust

emissions are the main pollution source, although plumes coming from the airport, harbour and industrial facilities can also contribute. The SMPS was deployed on the top of a building owned by the Queensland University of Technology (QUT), in an area considered as urban background (see Table S1). Previous work in the study area (Cheung et al., 2011) analysed one year of SMPS data in the ultrafine range, focusing on the nucleation processes in the urban background. They reported three main diurnal PN peaks; two related to traffic rush hours and a third one occurring at midday related to nucleation.

4) Rome (ROM), Italy: located 24 km inland from the Mediterranean Sea, it features 2.7 million inhabitants although the metropolitan area accounts for 4 million. The sampling site is located in Montellibreti, 30 km NE from the Rome city centre (Table S1). Although considered as a regional background site, it is regularly impacted by pollutants transported from the area of Rome, due to the sea-breeze circulation (Ciccioli et al., 1999). Previous work in the study area (Costabile et al., 2010) applied a clustering analysis (Principal Component Analysis, PCA) on two years of SMPS data, reporting three main factors: an aged nucleation mode, an Aitken mode and an accumulation mode factor (21%, 40% and 28% of the variance, respectively).

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5) Los Angeles (LA), USA: located on the Pacific coast of the United States, it is a metropolitan area that exceeds 15 million inhabitants. Road traffic, airplanes, shipping and manufacturing activities account for the highest contributions to air pollution. Smog periods are common in the Los Angeles Basin, caused by frequent atmospheric inversions. The SMPS data were sampled at the University of Southern California (USC) site (see Table S1). It is representative of the urban background environment and is influenced by traffic emissions from the I-110 freeway located 120 m to the west. A previous study (Hudda et al., 2010) analysed SMPS data sampled at this as one of several in the Los Angeles urban area. At the USC site two main PN peaks were observed coinciding with traffic rush hours and a third one at midday was attributed to secondary photochemical particle formation.

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Although the selected cities are located in similar climatic environments, some differences regarding meteorological conditions were encountered (see Table1). All cities show mild annual temperatures, ranging from 15ºC in Madrid (due to its inland location) to 20ºC in Brisbane (due to its latitude, closer to the equator, see Figure 1). Relative humidity varies by 10% across the cities, showing highest values in Brisbane (72%). This is probably related to the higher precipitation rate registered in this city (1072 mm), two times higher than in BCN, MAD or LA (430-450mm). As expected, the highest average annual values of solar radiation are recorded in Brisbane and the lowest in Madrid (240±337 Wm^{-2} and 182±265 Wm^{-2}, respectively). UFP concentrations (common size range 17.5-100 nm) showed lowest levels in Rome (due to the location of the sampling site, 5000±3000 cm^{-3}), followed by Brisbane, Madrid and Barcelona (6000±7000 cm^{-3}, 7000±8000 cm^{-3} and 7500±5000 cm^{-3}, respectively). The highest concentrations corresponded to the city of LA (12000±7000 cm^{-3}), probably due to the proximity to the freeway and the limited sampling time (3 months).

In addition to meteorological features, emission sources also have an impact on UFP in urban environments, especially traffic related pollutants. The vehicle fleet composition is not homogeneous among the sampling sites, as a tendency towards dieselization has been experienced in some European countries over the last years, especially in Spain (Amato et al., 2009), where 55% of vehicles are diesel-powered versus 44% gasoline (Dirección General de Tráfico, 2015). In Italy 37% of the vehicles used diesel fuel and 62% used gasoline in 2007 (Istituto Nazionali di Statistica, 2009). On the other hand, in the USA or Australia the diesel share represents only around 20% (Gentner et al., 2012; Australian Bureau of Statistics, 2014). Diesel vehicle engines are known to emit much higher PN than gasoline ones (Harris and Maricq, 2001), which might imply a higher concentration of primary UFP in European countries in comparison to the USA and Australia. Another relevant difference between the cities relates to their urban structure. While both Brisbane and Los Angeles are extensively suburbanised cities with relatively low population densities, favouring dilution and diffusion of pollutants, southern European cities are dense urban agglomerates that favour the trapping and accumulation of pollutants. The lower concentrations of UFP in Brisbane in comparison with European cities are therefore likely due to lower primary diesel emissions and higher precipitation rates, coupled with higher diffusion and dilution of pollutants due to the urban geography of the city. In the case of Madrid and Barcelona, the higher proportion of diesel vehicles together with the high urban density leads to an increase of UFP concentrations. In the case of Los Angeles, the high readings are probably due to both the proximity to the traffic source and the reduced sampling period (3 months). Given these differences between the cities, we nevertheless view the climatic similarities to be strong enough to consider the urban background environments in which the data have been sampled to be broadly comparable.

In order to show averaged annual results we only considered in this study the cities of Barcelona, Madrid and Brisbane for several reasons. In Rome, the sampling site is not located in an urban environment, although it is affected by the Rome pollution plume. Regarding Los Angeles only 3 months of measurements were available, which was not sufficient for studying the annual trends. In spite of these limitations, we are able to demonstrate from the data that the atmospheric processes affecting the other 3 cities do also occur in ROM and LA.

2.2 Measurements

2.2.1 Particle number size distributions

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The detailed characteristics of the sampling sites, sampling periods, SMPS models and size ranges at each city can be seen in Tables S1 and S2. The monitoring sites in the cities of Barcelona, Madrid, Brisbane and Los Angeles were classified as urban

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background, whereas the one in Rome was further away from the city. The SMPS low-cut point ranged from 10.2 nm to 17.5 nm whereas the SMPS high-cut point varied from 101.8 to 615.3 nm. The lack of measurements below 10 nm does not allow for proper identification of the start of new particle formation events, therefore our so-called "nucleation events" reflect photochemically nucleated particles that have grown over the low-cut detection limits of each instrument. In addition, such events were evaluated visually by inspecting the trends of the SMPS size distributions. More information reporting a detailed analysis of the aerosol size distributions used in this work can be found in previous studies (Madrid: Gómez-Moreno et al., 2011; Brisbane: Cheung et al., 2011; Rome: Costabile et al., 2010; Los Angeles: Hudda et al., 2010). Due to the different time resolution of each instrument, all measurements were averaged to 1 hour resolution. All data herein reported should be read as local time.

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2.2.2 Meteorological parameters and other air pollutants

Meteorological (temperature, relative humidity, wind components and solar radiation), gaseous pollutants (NO, NO_2, O_3, CO, SO_2) and other parameters (PM_x, PN, black carbon and particulate nitrate concentrations) were obtained at the site or from the closest available air quality station (see Table S3). These data were averaged to 1 hour resolution to match the SMPS measurements.

2.3 Data analysis (*k*-Means)

The large amount of data presented in this work (31,448 hours distributed across five sites) was simplified by applying *k*-Means clustering analysis (Beddows et al., 2009). This methodology has already been successfully applied to a number of studies involving one (Dall'Osto et al., 2012) or multiple monitoring sites (Dall'Osto et al., 2011; Brines et al., 2014). In a nutshell, this method creates manageable groups of clusters that can be classified into aerosol size distributions types (i.e. characteristic of emission or formation processes) and permits a simplification of the data analysis that facilitates its interpretation. To account for the uncertainty of the method, the confidence limits μ (99.9% confidence level) were calculated for all the cluster size distributions at each city, and uncertainty bands were plotted around each cluster size distribution. A detailed description of the method can be found in the supplementary information.

3 Results

3.1 *k*-Means clustering

A *k*-Means clustering analysis was performed on each of the five SMPS data sets, resulting in a number of representative clusters for each city that ranged between 7 and 15. After careful consideration, such results were further simplified to 4-7 clusters per monitoring site (see Figure 2b-d, 3b-c). For further information regarding cluster number reduction refer to the supplementary material. The uncertainty bands plotted for each cluster (Figs. 2b-d and 3b-c) show the 99.9% confidence limits for the hourly size distributions contained within each cluster. This means that with a probability of 99.9%, all hourly spectra contained in each cluster are found within the uncertainty bands. The fact that none of the uncertainty bands of the spectra overlap over the full size range at any of the sites reflects the robust cluster classification achieved by *k*-Means analysis. To further characterise each *k*-Means cluster, its corresponding size peaks were extracted; and hourly, weekly and annual cluster trends were analysed. Moreover, the corresponding average values of meteorological parameters and available air pollutants for each cluster at each site were calculated. The analysis of each cluster characteristics allows its classification into different categories depending on the main pollution source or process contributing to it.

The majority of the clusters were found common to most of the cities, although showing some site specific characteristics depending on the location of the site (proximity to pollution sources), the sampling size range (low-cut 10.2-17.5 nm and upper-cut 101.8-615.3 nm, see Table S2) and the particular emission and atmospheric features of each city (see Figs. 2b-d and 3b-c). To further simplify the results, the clusters have been carefully divided in four main categories: “Traffic”, “Background Pollution”, “Nucleation” and “Specific case”. The most relevant categories common to all sites are Traffic and Nucleation, which display very different characteristics. Broadly, Traffic clusters dominate the aerosol size distributions during rush hours, showing very high NO_x levels. In contrast, Nucleation clusters are seen at midday, under high temperature, solar radiation and ozone levels and low NO_x levels. Detailed features of each *k*-Means size distributions can be found in Table 2, S4, S5, S6 and Figures 2 and 3. Finally, it is important to remember that the clustering results can provide a much higher amount of information than that presented here. Nevertheless, the objective of this study is to present four main aerosol size distribution categories in order to quantify the impact of photochemical nucleation processes in urban environments under high solar radiation. Therefore, the following results are focused on the cities of Barcelona, Madrid and Brisbane, whereas the data from Rome and Los Angeles due to the limitations they present (site location and limited data availability, respectively) will be used only to complement the discussion.

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3.1.1 Traffic-related clusters

- Traffic 1 (T1): this cluster can be seen at all monitoring sites, occurring 27-24% of the time (Table S4). It exhibits a bimodal size distribution, as typically found in vehicle

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exhausts, with a dominant peak at 20-40 nm (traffic-related nucleated particles) and another at 70-130 nm (soot particles) (see Table 2). Its diurnal trends are driven by traffic rush hours and display very high levels of traffic pollutants, such as NO, NO_2, BC and CO (see Fig. S1a and S2). Regarding particle mass concentrations, T1 is associated with high values of PM_{10} (see Fig. S2). We attribute this cluster to freshly emitted traffic particles.

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- Traffic 2 (T2): this cluster is seen in Barcelona and Madrid, occurring 22-24% of the time (Table S4). It shows a bimodal size distribution with a minor peak at 20-40 nm and a dominant one at 70-90 nm (see Table 2). It is usually observed during the evening and night, and contains high concentration of traffic pollutants, like T1 (see Fig. S1a and S2). The main difference with T1 is that it accounts for particles with traffic origin that might have undergone physicochemical processes after being emitted, such as condensation or coagulation and that have resulted in a change of the size distribution with respect to T1. This change can be appreciated for each city in Figure 2.

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- Traffic 3 (T3): this traffic related cluster was found in all the monitored cities 11-20% of the time (see Table S4). It presents a bimodal size distribution, with a low peak in the nucleation mode at 10-20 nm and a main peak at 50-90 nm (see Table 2). It occurs throughout all day, with a peak during daytime, and it is associated with the lowest pollution levels of all the Traffic clusters (see Fig. S1a). The shift to smaller sizes of the 20-40 nm peak of T1 and T2 towards the nucleation mode in T3 might indicate particle evaporation in Barcelona, Madrid and Brisbane (see Fig. 2b, c, d) (Dall'Osto et al., 2011). More information on the evolution of traffic related cluster T1-T2 towards traffic related cluster T3 can be found in Brines et al. (2014), where aerosol size distribution modes simultaneously detected at four monitoring sites during SAPUSS were reported.

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3.1.2 Background pollution clusters

- Urban Background (UB): the Urban Background cluster can be observed at all 3 sites 6-22% of the time (see Table S4). The size distributions present a bimodal peak at 20-40 nm and at 60-120 nm (see Table 2). At Barcelona and Madrid - cities highly influenced by road traffic emissions - the dominant peak is the finest one, whereas in Brisbane the larger peak prevails (see Table 2). Urban background clusters were usually observed during the night time, associated with relatively clean atmospheric conditions in the urban environment (see Fig. S1a and S2).

- Summer Background (SB): this cluster occurred 7% of the time in Madrid (see Table S4). The unimodal size distribution shows a peak in the Aitken mode at 44±1 nm (see Table 2). It is seen during the summer nights and thus influenced by low levels of traffic pollutants, pointing towards clean summer atmospheric conditions.

3.1.3 Nucleation cluster

- Nucleation (NU): the Nucleation cluster was found to be common to all sites - stressing the importance of the occurrence of new particle formation processes in high insolation urban environments (see Table S4). It occurs for between 14 and 19% of the measured periods and has a dominant nucleation mode peak in the range 10-20 nm and a minor size peak in the Aitken mode at 50-80 nm (see Table 2), the latter being attributed to background aerosols. It is observed at midday or early afternoon more intensively during spring and summer (see Fig. S1b). It is generally characterised by very high solar irradiance, high wind speed and low concentration of traffic pollutants (see Fig. S2).

3.1.4 Specific case clusters

- Nitrate (NIT): this cluster was observed in the two Spanish cities, occurring 7% of the time in Barcelona and 10% of the time in Madrid. This cluster is characterised by its

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Eliminado: - Regional Background (RB): this cluster was found specific to the Rome sampling site, occurring 28% of the time (see Table S4). Its size distribution displays a peak at 89±1 nm, probably indicating aged Aitken mode aerosols from road traffic and nucleation sources (see section 3.2 and Fig. 3c). It is seen especially during the winter nights. It reflects the regional characteristics of the Montelibretti site and corresponds to the Regional Background PCA factor described in Costabile et al. (2010). ¶
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prevalence at night during the colder months (see Fig. S1b). Moreover, in Madrid a minor peak was also seen during midday. Although the Nitrate cluster occurs more frequently at night, photochemically induced nitrate formation accounts for higher mass concentrations during the day, especially in winter in Madrid (Gómez-Moreno et al., 2007; Revuelta et al., 2012).

The two size distributions associated with nitrate in Barcelona and Madrid are unimodal although presenting different modes. BCN_NIT shows a finer mode at 36±1 nm, whereas MAD_NIT shows a larger size mode at 63±1 nm. This might be due to the location of the sampling sites, closer to traffic sources in Barcelona (urban background) than in Madrid (suburban background).

- Growth 1 and 2 (G1, G2): these clusters were found exclusive to the Brisbane monitoring site and both accounted for 10% of the time. They show a unimodal peak at 28±1 and 37±1 nm, respectively. These are frequently seen in the afternoon after photonucleation occurs (BNE_G2 follows BNE_G1), and are likely related to further growth of nucleated or traffic particles (see section 3.2 and Fig. 3d).

3.2 *k*-Means clustering results explained by the cluster proximity diagram

Another way of looking at the *k*-Means results is through the Cluster Proximity Diagram (CPD), which is obtained using the Silhouette Width (Beddows et al., 2009). This diagram positions each cluster according to the similarity with the rest of the clusters (Figure 2e-g).

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The closer nodes represent similar clusters, although they are not sufficiently alike to form a new cluster. Conversely, the more distant nodes represent the most dissimilar clusters and are located further apart. The average cluster modal diameter increases from left to right.

Figure 2e-g shows the corresponding CPDs for the main selected cities. The Nucleation clusters NU are located in the far left side of the diagram, as they account for a very fine

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size mode (see Table 2). Traffic clusters (T1-T3) are positioned next to NU, although their location within the CPD varies depending on the city. In general, T3 and T1 are confined closer to the NU clusters than T2, given their association with primary traffic emissions (T1) and evaporation of traffic particles or nucleation (T3). Clusters T2 are an intermediate step between fresh traffic emissions (T1) and the Urban Background clusters (UB). Regarding the Background Pollution clusters (UB and SB), their location on the right side of the graphs suggests that the sources/processes loading the Nucleation and Traffic clusters develop and contribute to this category. Barcelona and Madrid (Figs. 2e and 2f, respectively) show site specific clusters. The SB cluster in Madrid is loaded with traffic particles from T1 and T2 before it contributes to the Nitrate (NIT) cluster. Other site specific clusters such as Nitrate (NIT) are only observed in Barcelona and Madrid (Figs. 2e and 2f, respectively). In the case of Barcelona, NIT is linked to the Traffic clusters T1 and T2, highlighting its urban nature. On the other hand, although the Traffic clusters T2 and T3 contribute to the formation of Nitrate in Madrid, both Background Pollution clusters UB and SB add to its loading, thus resulting in a higher modal diameter for the NIT cluster in Madrid than in Barcelona (Table 2). The remaining Growth clusters in Brisbane (G1 and G2) are positioned in the centre of the CPD (Fig. 2f) and represent particle growth from NU or the Traffic clusters (T1 and T3) before contributing to the UB. This is also supported by their time occurrence after the NU or T clusters.

3.3 *k*-Means clusters of Rome and Los Angeles

Both Rome and Los Angeles clusters were classified into the same categories as the main cities, thus similar characteristics regarding meteorological parameters and gaseous pollutants as in the main cities apply. Due to its location in a regional background area under the influence of the Rome pollution plume, the Rome clusters showed some differences with respect to those of Barcelona, Madrid and Brisbane. For Rome, the Traffic

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(T1-T3) and Nucleation clusters displayed a lower occurrence (41% and 6%, respectively) as well as a shift in its peaks to larger sizes, reflecting their aged nature (see Tables S5, S6). Indeed, previous studies have showed that an aged nucleation mode of particles in the size range 20-33nm is related to photochemically nucleated particles downwind of Rome growing in size while being transported to the sampling site (Costabile et al., 2010). Moreover, in addition to the Urban Background cluster, a unique Regional Background cluster occurring 28% of the time (Table S4) was found specific to this site, and corresponded to the Regional Background PCA factor described in Costabile et al. (2010). Regarding Los Angeles, although this site was located in an urban background environment, aerosol size distributions were only measured from September to December (see Table S2). Two Traffic clusters and an Urban Background cluster were identified (representing 61% and 6% of the time, respectively), reflecting the proximity of the sampling site to main roads. The Nucleation cluster was found to occur 33% of the time, due to the enhancement of photochemical nucleation events during warm months (see Table S4).

4 Discussion

The results described in section 3.1 (for the cities of BCN, MAD and BNE) can be summarised and simplified in the following categories:

- Traffic. This category includes all clusters directly related to traffic emission sources. It contains 3 subcategories (Traffic 1-Traffic 3) ranging from fresh traffic emissions to aerosols that have been affected by atmospheric processes after emission, such as coagulation, condensation or evaporation (Dall'Osto et al., 2011). This is the dominant category at all sites, showing the high prevalence of traffic emissions in the ultrafine PN

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Eliminado: except for Rome (site located outside the city) concentration in urban background sites. This category was found to be the main one in all the studied cities, ranging from 44% in Brisbane to 63% in Barcelona (see Table 3). The average Traffic size distribution shows a main peak in the Aitken mode at 31±1 nm and a minor one in the accumulation mode at 120±2 nm (see Figure 4 and Table 4). According to vehicle emission studies, the Aitken mode corresponds with grown nucleated particles associated with the dilution of vehicle exhausts (Kittelson et al., 2006; Ntziachristos et al., 2007), while the larger mode is associated with solid carbonaceous compounds from exhausts (Shi et al., 2000; Harrison et al., 2011). The clusters included in this category are characterised by the highest levels of traffic-related pollutants, such as NO, NO_2, CO and BC. These values are usually higher for clusters T1 and T2 and decrease for T3 (see Fig. S2).

- Background Pollution. These clusters characterise the urban background and regional background pollution of the sites. They are likely composed of a mixture of aerosol particle types with different sources and origins. They usually describe the cleanest conditions encountered at the urban sites, ranging from 13 to 22% of the time (see Table 3). The resulting average spectra for all background clusters (Figure 4) show a trimodal size distribution, with two peaks in the Aitken mode (at 38±3 nm and 72±2 nm) and a minor one in the accumulation mode at 168±14 nm, reflecting aged aerosols mostly of an anthropogenic origin (see Table 4).

- Specific case. These clusters are associated with "Nitrate" containing aerosol particles, and "Growth" of new particle formation events. The Nitrate cluster was observed in Madrid and Barcelona, whereas the Growth clusters were only seen in Brisbane. Each cluster represents around 10% of the time at their respective sites (see Table 3). The difference in

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the Nitrate size distributions of Barcelona and Madrid might be due to the urban site characteristics of this cluster in Barcelona, while in Madrid it is also enriched with Background clusters (see Figure 2b-c). The Growth clusters reflect the size mode increase of nucleation particles due to subsequent growth (see Table 2), since they are recorded after nucleation episodes.

- Nucleation events. Nucleation events account for 14-19% of the hourly observations, with an average of 16% of the time, indicating nucleation as an important source of UFP in high insolation urban areas (see Table 3). The average Nucleation size distribution (Figure 4) is characterised by a high PN nucleation mode peak at 17±1 nm and a lower PN peak in the Aitken mode at 53±7 nm (Table 4). It occurs under intense solar irradiance, clean air conditions (high wind speed and low concentrations of CO, NO and NO_2), low relative humidity and relatively high levels of SO_2, although still low SO_2 levels in absolute concentration values (see Fig. S2). It presents the highest PN (12000±8000 cm^{-3}) of all categories (see Figure 4). The PN/NO_x ratio from 8 a.m. to 12 a.m. was calculated for the Nucleation and Traffic 1 clusters for each city. In all cases it was found to be higher for the Nucleation than for the Traffic 1 clusters, highlighting both the clean atmospheric conditions favouring nucleation (low NO_x levels) and the contribution of nucleated particles to PN. In summary, this study shows that new particle formation events can be an important source of UFP in urban areas under high solar radiation, as it is the dominant particle number concentration source on average for 16% of the time. This is also reflected in the average PN daily profiles, calculated using the respective SMPS total PN concentrations during the whole study period for each city (Figure S3). Indeed, in cities like Barcelona, Brisbane and Los Angeles a clear midday peak between the two rush hour peaks (morning and evening) is observed. In the case of Madrid, the nucleation peak coincides with a decrease in PN at the end of the morning rush hour, while in Rome a

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Eliminado: This variability might be due to the sampling period (during autumn in Los Angeles, when photonucleation is intense, see Hudda et al., 2010) or location and the reduced number of grown nucleated particles downwind of Rome that reach the sampling site at Montelibretti (Costabile et al., 2010). Excluding Rome (6%) and Los Angeles (33%) the occurrence of nucleation events in the remaining cities is 14-19% of the time.

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minor peak can be observed around 3 p.m., when the nucleated particles downwind of Rome reach the sampling site. The occurrence of an increase in PN levels related to photochemical nucleation events at midday in specific Spanish cities has already been reported by Reche et al. (2011). However, we show that this trend is common to worldwide cities sharing a temperate climate and high solar radiation levels. Furthermore, this study shows that new particle formation events in high insolation urban environments often fail to grow to sizes larger than 30-40 nm (Figure 5a-c and Figure 6). In order to analyse this, we link our discussion to that reported in Dall´Osto et al. (2013). At least two main different types of new particle formation events can be seen in the Mediterranean urban environment:

(1) A regional type event, originating in the whole study region and impacting almost simultaneously the city and the surrounding urban background area;

(2) An urban type event, which originates only within the city centre but whose growth continues while transported away from the city to the regional background.

The main difference between these two types resides in the origin of the nucleation events (regional scale in type 1 and urban origin in type 2). Moreover, the regional events are found to start earlier in the morning than the urban type and usually display the typical banana shape implying that photochemically nucleated particles experience subsequent growth. On the other hand, the urban type nucleated particles experience less growth, reaching sizes of 30-40 nm. The city of Brisbane exhibits new particle formation events starting in the morning (see Figure 5c), similar to the regional nucleation event types discussed in Dall´Osto et al. (2013). This may be due to the fact that the Brisbane site was located in a relatively clean environment. By contrast we find that the majority of new

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particle formation events detected in the other cities occur under the highest solar irradiance and thus around noon. Such events are characterised by a burst of particles lasting for about 3-4 h. A typical example is seen in Fig 5a. In the case of Madrid, there is no clear separation between the morning rush hour traffic-related particles (20-100nm in size) and the nucleation particle burst at noon (20-40 nm), (Fig. 5b). This might be due to the similar PN concentrations exhibited by MAD_T1, MAD_T2 and MAD_NU clusters (see Fig.2c). The average diurnal PN considering Barcelona, Madrid and Brisbane size distributions (Fig. 6) shows that the typical nucleation event detected in urban environments consists of a particle burst that grows up to 20-40 nm in size. It occurs under high solar irradiance and temperature, and low relative humidity and NO_x levels. It also coincides with the development of the boundary layer and the dilution of road traffic emitted pollutants. Further growth of these nucleated particles in urban environments following a banana-like shape is probably constrained by the decrease in solar radiation intensity and the prevalence of traffic emitted particles in the evening.

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Although only 3 months of data are available, the same conclusion can be extracted from the urban LA site, whereas aged nucleated particles downwind of Rome (20-40 nm) reach the Rome regional site in the early afternoon (Fig 5d-e). Indeed, previous studies reported that the sea breeze regime favoured the transport of photochemically transformed pollutants such as nucleated particles from the urban and suburban area downwind of Rome to the sampling site (Ciccioli et al., 1999; Costabile et al., 2010). This phenomenon has also been reported for the city of Barcelona by Dall'Osto et al. (2013), where several hours after the occurrence of a nucleation event originating in the city of Barcelona, a particle burst of 20-40 nm in size was detected at a regional site located 50 km downwind of the city centre, reflecting the growth of the nucleated particles while being transported away by the sea breeze.

It is common in the literature to refer to the frequency of nucleation events as the percentage of days such an event has been detected. The size distribution time series need to be visually inspected to certify that a distinct new mode starting in the nucleation range appears, that the mode prevails over some hours and that it shows signs of growth (Dal Maso et al., 2005). This methodology has been proven to be very useful to detect banana-like nucleation events, where distinct nucleation events and subsequent particle growth can be observed. However, this is not the most common nucleation event type detected in the studied urban environments, where an increase in the condensation sink due to road traffic emissions might constrain the growth of nucleated particles growth. Instead nucleation events consist on particle bursts lasting for 3-4 hours with particle growth limited to 20-40 nm (see Fig. 5 and 6). Therefore, to adapt this methodology to our current scenario, the percentage of days that presented nucleation events were classified considering the prevalence of the Nucleation cluster from 2 up to 4 consecutive hours for each site. The results were found to be very homogeneous among the main sampling sites (see Table 5). Nucleation events were detected for 53-58% of the days lasting for two hours or more, decreasing to 37-43% for 3 hours or more and 27-30% for 4 hours or more. The decrease in occurrence of long nucleation events is a consequence of the limitation for nucleated particles to grow in high insolation urban environments. Interrupted nucleation events were not considered, which may have led to slightly higher occurrence if considered.

The urban nucleation events described in this paper presumably have an anthropogenic origin, or at least be influenced by anthropogenic precursors, due to the fact that such events are seen initiating in city hot spots and not in the nearby background (Dall´Osto et al., 2013). Betha et al. (2013) reached the same conclusion regarding urban nucleation episodes in a tropical environment (Singapore). This has important implications because the city seems to be not only a source of primary UFP but also a driver for nucleation events occurring only in the city. Little is known about health effects of UFP in urban areas (HEI Overview Panel, 2013), the possible mechanisms and chemical components responsible for such events, or if there are differences in health impact between the two nucleation event types discussed here. Given that we are still in the early satges of our understanding of the toxicology and epidemiology of urban UFP, adoption of the precautionary principle in attempting to reduce such emissions would seem wise.

5 Conclusions

With the aim of evaluating the nature and impact of urban nucleation events on levels of ambient UFP in high insolation urban environments, we apply a unified specialized tool to long term data sets (1-2 years) sampled at several cities. Size resolved particle measurements were performed in three urban background environments in high insolation regions: Barcelona, Madrid and Brisbane. Measurements from Rome and Los Angeles were also included to complement the study. Individual studies have demonstrated the occurrence of urban nucleation events in certain cities; however this is the first study that systematically assesses such events in worldwide cities with a similar climate. To this end a *k*-Means clustering analysis was performed on each data set, summarised in four main categories: “Traffic”, “Background Pollution”, “Nucleation” and “Specific case”. Although the main source of UFP was attributed to road traffic emissions (representing 44-63% of the time), photochemical nucleation events accounted on average for 16% of the observations, being a relevant source of UFP in high insolation urban environments. This is reflected in the midday peak of daily average PN levels recorded at many of the study cities due to nucleation events, although most of these events were not followed by growth, with most of the detected events lasting about 1-4 hours and reaching sizes of about 30-40 nm. At least two different new particle formation events were classified: one starting in the morning at about 9-12 a.m., and a second one starting in the afternoon at

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Eliminado: The Australian city of Brisbane was also included due to its climatic similarities.

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about 1-4 p.m. (Dall´Osto et al., 2013). Both events did not last more than 3-6 hours, indicating the urban environment is not one that allows full growth of particles as seen in the more remote regional background. On average, nucleation events lasting for 2 hours or more were detected in 55% of the days, this extending to over 4 hours in 28% of the days, demonstrating that the atmospheric conditions in urban environments do not favour photochemically nucleated particles growth.

Eliminado: s

Eliminado: Nevertheless,

Eliminado: it remains an important source of UFP in the urban Mediterranean atmosphere.¶
¶

Acknowledgements

The authors would like to thank Dr. Cristina Reche and Dr. Noemí Pérez for supporting the ancilliary data of Barcelona and for their valuable help in the correct functioning of the SMPS. The gaseous pollutant data for Barcelona were supported by Meteocat and the meteorological data by the Faculty of Physics of the University of Barcelona. Ángeles Cristobal from Ayuntamiento de Madrid is also acknowledged for providing the data of Casa de Campo (Madrid). This study was partially funded by the VAMOS project (CGL2010-19464) regarding Barcelona measurements. MICROSOL project (CGL2011-27020) has partially funded this research and Madrid measurements. This study was partially supported by the Australian Research Council through Discovery Project Grant DP0985726. The data in Los Angeles were funded by the South Coast Air Quality Management District (SCAQMD) (award #11527) and the USC Provost's Ph.D. fellowships.

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TABLE LEGENDS

Table 1: Average annual meteorological parameters for each site during the respective study periods. Due to the reduced data availability in LA, values in brackets represent annual values provided by NOAA or NASA.

Table 2: Log-Normal fitting peaks for each cluster category *k*-Means size distribution at the main sites and the corresponding peak area percentage.

Eliminado: 1

Eliminado: each site

Table 3: Cluster categories (Traffic, Background, Nucleation and Specific case (SC)) and their occurrence at the main sites.

Eliminado: 2

Eliminado: each

Table 4: *k*-Means cluster categories average size distribution size mode peaks and corresponding area percentage. Only the main cities BCN, MAD and BNE were considered.

Eliminado: 3

Table 5: Percentage of nucleation event days at the main cities BCN, MAD and BNE, and the uninterrupted time prevalence of these events.

FIGURE LEGENDS

Figure 1: Location of the cities selected for the study. The 3 main cities Barcelona (BCN), Madrid (MAD) and Brisbane (BNE) are marked in red. The supporting cities of Los Angeles (LA) and Rome (ROM) are shown in orange. The green areas delimit the regions with temperate climate (class C) according to the Köppen classification. The cities of BCN, MAD, ROM and LA are in Mediterranean climate regions (type Csa/b, light green), whereas BNE has a humid subtropical climate (type Cfa, dark green). Image source: Wikimedia.

Figure 2: Aerosol size distribution results of the *k*-Means cluster analysis performed on the SMPS data at each selected city: a) legend, b) Barcelona, c) Madrid, d) Brisbane. Shaded areas around the curves represent the confidence limits µ calculated for 99.9% confidence level. Please note the different scales for dN/dlogD$_p$. The corresponding Cluster Proximity Diagram (CPD) is shown for the 3 main selected cities: e) Barcelona, f) Madrid and e) Brisbane.

Eliminado: 3 sigmas

Figure 3: Aerosol size distribution results of the *k*-Means cluster analysis performed on the SMPS data at the selected complementary cities: a) legend, b) Rome and c) Los Angeles. Shaded areas around the curves represent the confidence limits calculated for 3

Eliminado: each

Eliminado: y

Eliminado: Barcelona

Eliminado: ,

Eliminado: Madrid

Eliminado: , d) Brisbane.

sigmas. Please note the different scales for dN/dlogD$_p$. Cluster proximity diagrams shown for both cities: d) Rome and e) Los Angeles.

Figure 4: Average aerosol size distributions for each *k*-Means cluster category: Traffic, Background and Nucleation. Only the main cities BCN, MAD and BNE were considered.

Figure 5: Mean SMPS size distributions on a nucleation day at each selected city, NO$_x$ average concentration and the frequency of occurrence of the Nucleation cluster for: a) Barcelona, b) Madrid, c) Brisbane, d) Rome and e) Los Angeles. Please note that NO$_x$ concentrations for Madrid represent NO$_x$/2 and for Los Angeles NO$_x$/10. These values are 30-65% lower on nucleation days than the corresponding sampling period average levels.

Eliminado: Rome,

Eliminado: Brisbane

Figure 6: Daily average PN size distribution, temperature, relative humidity, solar radiation and NO$_x$ levels on a nucleation day using data from Barcelona, Madrid and Brisbane.

Eliminado: , Rome

Table 1: Average annual meteorological parameters for each site during the respective study periods. Due to the reduced data availability in LA, values in brackets represent annual values provided by NOAA or NASA.

City	T (ºC)	RH (%)	Rain (mm)	Solar radiation (Wm^{-2})	PN$_{17.5-100nm}$ (cm^{-3})
Barcelona	18±6	68±16	432	190±270	7500±5000
Madrid	15±7	66±23	438	182±265	7000±8000
Brisbane	20±5	72±20	1072*	240±337	6000±7000
Rome	19±7	59±17	732[#]	203±274	5000±3000
Los Angeles	19±6 (19[$])	58±20 (71[$])	126 (452[$])	(225[+])	12000±7000

* Australian Government Bureau of Meteorology

[#] http://www.weatherbase.com/weather/weatherall.php3?s=124261&refer=&units=metric

[$] National Oceanic and Atmospheric Admisnistration (NOAA)

[+] National Aeronatics and Space Sdmisnistration (NASA)

Table 2: Log-Normal fitting peaks for each cluster category *k*-Means size distribution at the main sites and the corresponding peak area percentage.

Category	Subcategory	Barcelona	Madrid	Brisbane
Traffic	Traffic 1 (T1)	26±1 nm (84%), 130±4 nm (16%)	25±1 nm (31%), 70±6 nm (69%)	21±1 nm (30%), 77±1 nm (70%)
	Traffic 2 (T2)	23±2 nm (31%), 36±1 nm (8%), 75±2 nm (61%)	31±3 nm (30%), 83±9 nm (70%)	-
	Traffic 3 (T3)	11±1 nm (21%), 48±1 nm (79%)	21±1 nm (24%), 92±3 nm (76%)	14±1 nm (18%), 52±4 nm (82%)
Background	Urban Background (UB)	22±1 nm (61%), 96±1 nm (39%)	40±1 nm (53%), 119±1 nm (47%)	63±2 nm (100%)
	Summer Background (SB)	-	44±1 nm (100%)	-
	Regional Background (RB)	-	-	-
Nucleation	Nucleation (NU)	16±1 nm (53%), 69±2 nm (47%)	19±1 nm (24%), 48±2 nm (76%)	13±1 nm (74%), 77±1 nm (26%)
Specific case (SC)	Nitrate (NIT)	36±1 nm (100%)	63±1 nm (100%)	-
	Growth 1 (G1)	-	-	28±1 nm (100%)

Eliminado: ¶

Eliminado: 1

Eliminado: each site

	Growth 2 (G2)	-	-	37±1 nm (100%)

Table 3: Cluster categories (Traffic, Background, Nucleation and Specific case (SC)) and their occurrence at the main sites.

Eliminado: 2

Eliminado: each

Category	Barcelona	Madrid	Brisbane
Traffic	63%	58%	44%
Background	15%	13%	22%
Nucleation	15%	19%	14%
SC: Nitrate	7%	10%	-
SC: Growth	-	-	20%
	100%	100%	100%

Table 4: *k*-Means cluster categories average size distribution size mode peaks and corresponding area percentage. Only the main cities BCN, MAD and BNE were considered.

Eliminado: 3

Category	nucleation	Aitken	accumulation
Traffic	-	31±1 nm (86%)	120±2 nm (14%)
Background	-	38±3 nm (71%), 72±2 nm (25%)	168±14 nm (4%)
Nucleation	17±1 nm (43%)	53±7 nm (57%)	-

Table 5: Percentage of nucleation event days at the main cities BCN, MAD and BNE, and the uninterrupted time prevalence of these events.

City	2 h or more	3 h or more	4 h or more
Barcelona	54%	43%	28%
Madrid	58%	41%	30%
Brisbane	53%	37%	27%

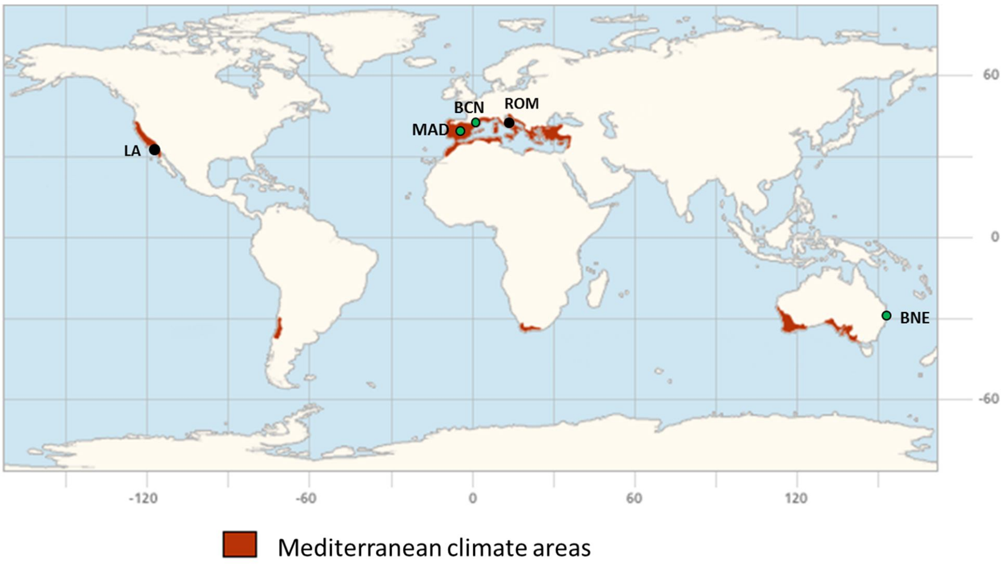

Figure 1: Location of the cities selected for the study. The 3 main cities Barcelona (BCN), Madrid (MAD) and Brisbane (BNE) are marked in green, whereas the supporting cities of Los Angeles (LA) and Rome (ROM) are shown in black. The cities of BCN, MAD, ROM and LA are located in Mediterranean climate regions, whereas BNE has a humid subtropical climate. Image source: US National Park Service California Mediterranean Research Learning Center.

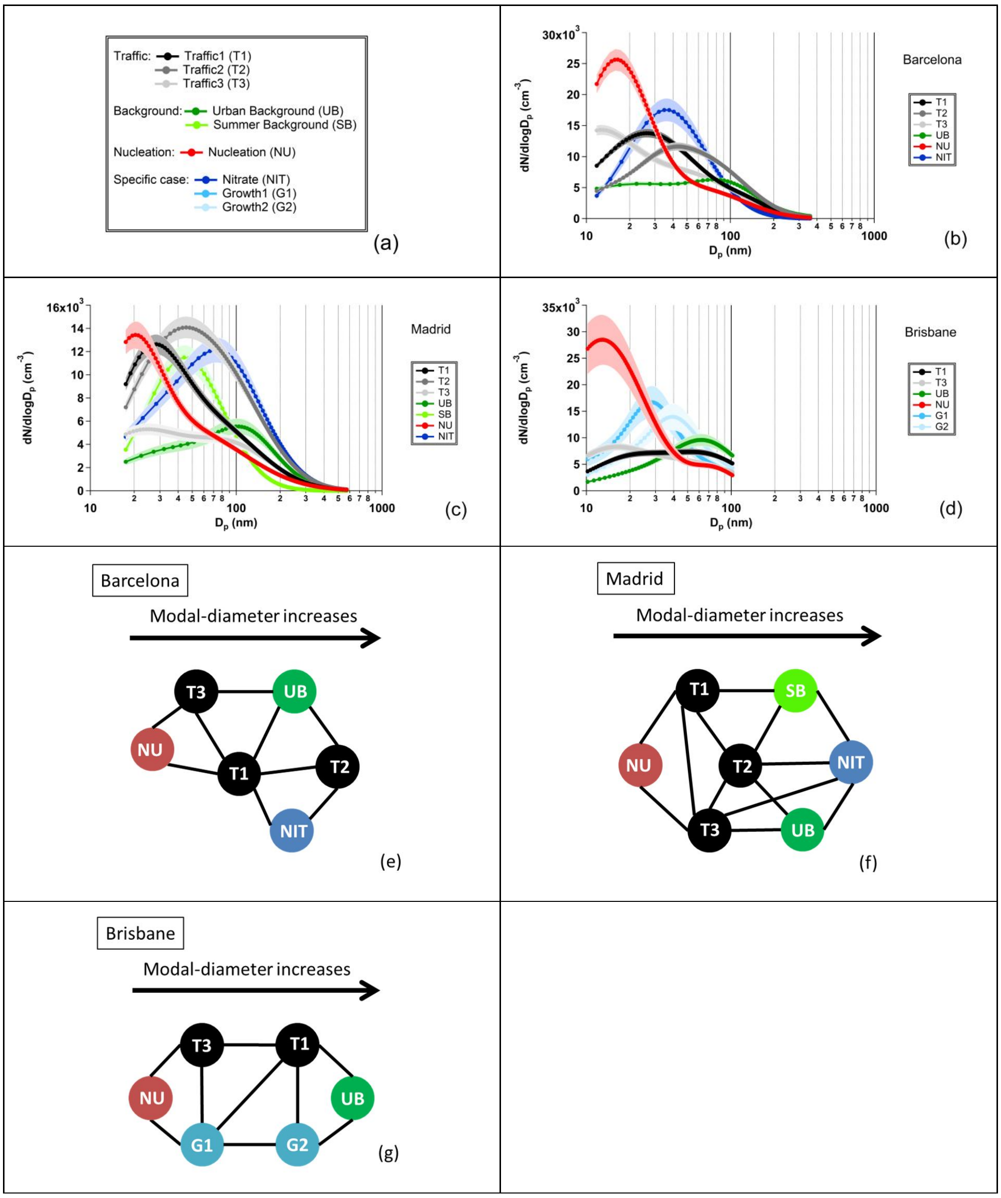

Figure 2: Aerosol size distribution results of the *k*-Means cluster analysis performed on the SMPS data at each selected city: a) legend, b) Barcelona, c) Madrid, d) Brisbane. Shaded areas around the curves represent the confidence limits μ calculated for 99.9% confidence level. Please note the different scales for $dN/dlogD_p$. The corresponding Cluster Proximity Diagram (CPD) is shown for the 3 main selected cities: e) Barcelona, f) Madrid and g) Brisbane.

Eliminado: 3 sigmas

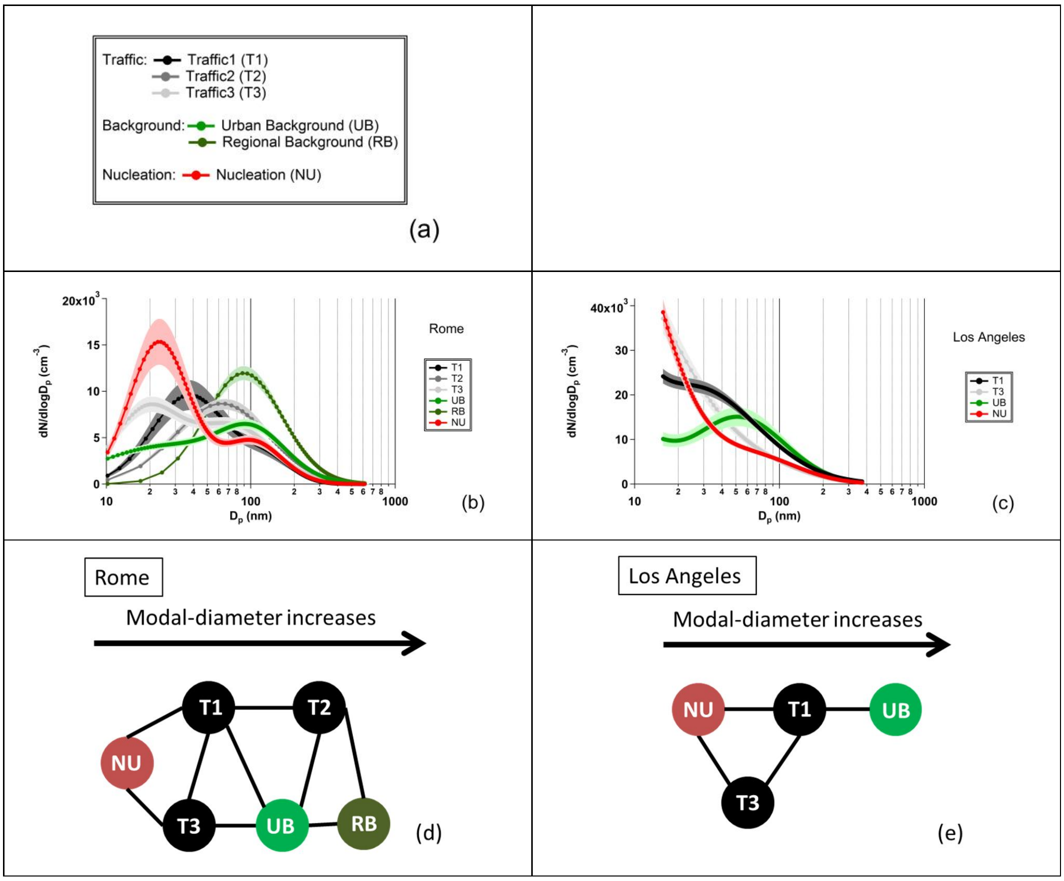

Figure 3: Aerosol size distribution results of the *k*-Means cluster analysis performed on the SMPS data at the selected complementary cities: a) legend, b) Rome and c) Los Angeles. Shaded areas around the curves represent the confidence limits calculated for 3 sigmas. Please note the different scales for dN/dlogD$_p$. Cluster proximity diagrams are shown for both cities: d) Rome and e) Los Angeles.

Eliminado: each

Eliminado: y

Eliminado: Barcelona

Eliminado: ,

Eliminado: Madrid

Eliminado: , d) Brisbane.

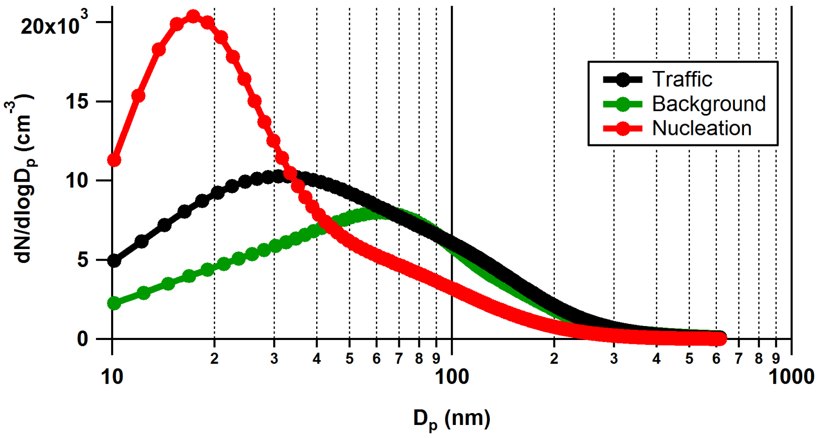

Figure 4: Average aerosol size distributions for each *k*-Means cluster category: Traffic, Background and Nucleation. Only the main cities BCN, MAD and BNE were considered.

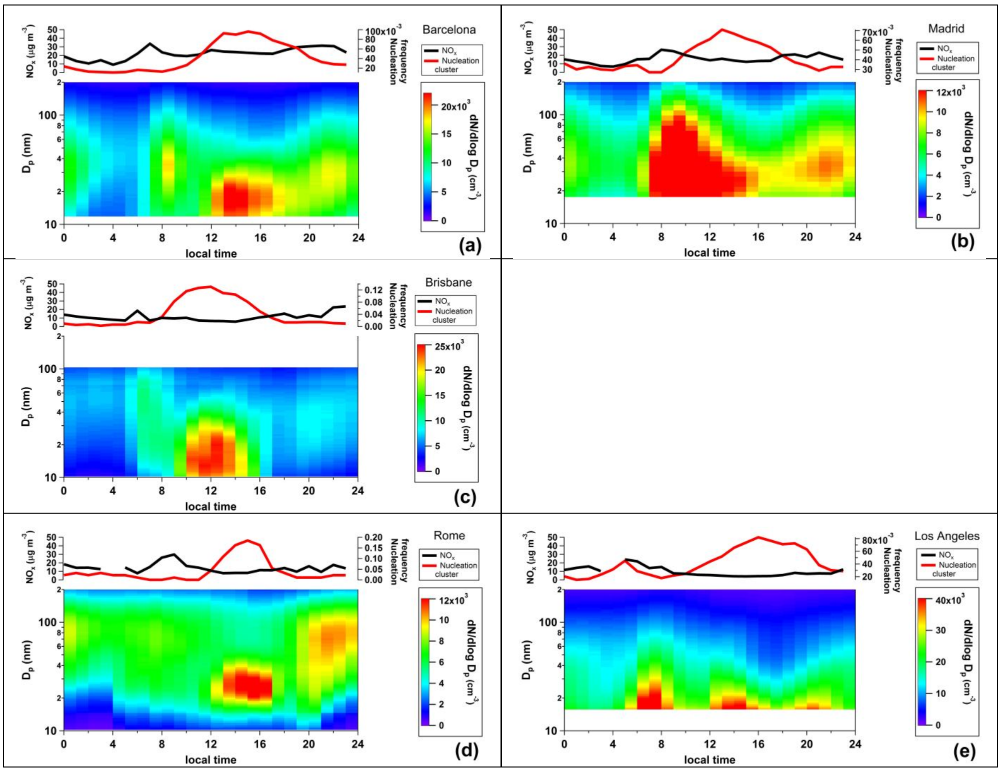

Figure 5: Mean SMPS size distributions on a nucleation day at each selected city, NO_x average concentration and the frequency of occurrence of the Nucleation cluster for: a) Barcelona, b) Madrid, c) Brisbane, d) Rome and e) Los Angeles. Please note that NO_x concentrations for Madrid represent $NO_x/2$ and for Los Angeles $NO_x/10$. These values are 30-65% lower on nucleation days than the corresponding sampling period average levels.

Eliminado: Daily average

Eliminado: Rome,

Eliminado: Brisbane

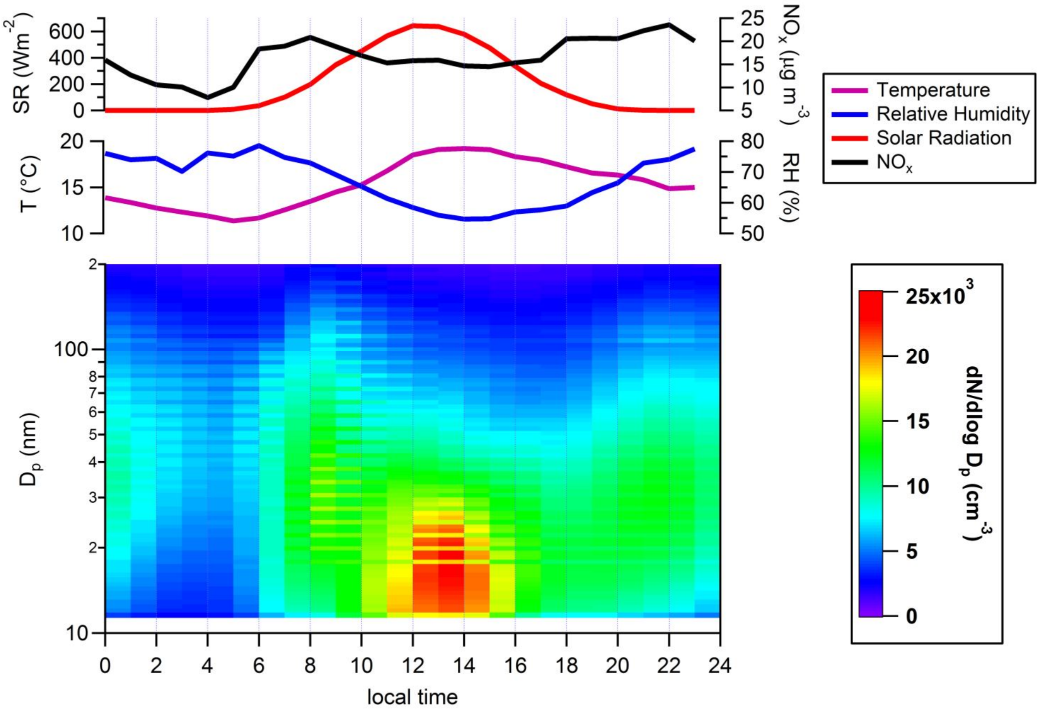

Figure 6: Daily average PN size distribution, temperature, relative humidity, solar radiation and NO_x levels on a nucleation day using data from Barcelona, Madrid and Brisbane

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Eliminado: , Rome