Traffic and nucleation events as main sources of ultrafine particles in high insolation developed world cities

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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 (Spain), Madrid (Spain) and Brisbane (Australia). Three long term datasets (1-2 years) of fine and ultrafine particle number size distributions (measured by SMPS, Scanning Mobility Particle Sizer) were analysed. Compared to total particle number concentrations, aerosol size distributions offer far more information on the type, origin and atmospheric evolution of the particles. By applying *k*-Means clustering analysis, we categorized the collected aerosol size distributions in three main categories: “Traffic” (prevailing 44-63% of the time), “Nucleation” (14-19%) and “Background pollution and Specific cases” (7-22%). Measurements from Rome (Italy) and Los Angeles (California) 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. On average, nucleation events lasting for 2 hours or more occurred on 55% of the days, this extending to >4hrs in 28% of the days, demonstrating that atmospheric conditions in urban environments are not favourable to the growth of photochemically nucleated particles. In summary, although traffic remains the main source of UFP in urban areas, in

developed countries with high insolation urban nucleation events are also a main source of UFP. If traffic-related particle concentrations are reduced in the future, nucleation events will likely increase in urban areas, due to the reduced urban condensation sinks.

1 Introduction

Largely populated urban areas are hotspots of urban air pollution due to the many and highly complex pollution sources of particulate matter and gaseous co-pollutants. Current regulations address the amount of ambient particulate matter expressed as a mass concentration of particles, and not particle number concentrations. However, the European Union (EU) has recently taken initial steps to set particle number concentrations emission regulations for vehicular emissions (EU, 2012). It is worthy of note that ultrafine particles - the main source of particles by number - are ubiquitous in urban environments (Kumar et al., 2014), and typically are of 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). There is increasing scientific evidence that removal of particles deposited in the lung is size-related (Salma et al., 2015). A number of studies have focused on the source apportionment of number and size characteristics of submicron particles in urban ambient air (Pey et al., 2009; Costabile et al., 2009; Harrison et al., 2011; Dall´Osto et al., 2012; Hussein et al., 2014; Liu et al., 2014; Salimi et al., 2014).

The main source of primary ultrafine particles in urban area is traffic activity. These particles can be formed in the engine or in the atmosphere after emission from the tailpipe (Shi and Harrison, 1999; Charron and Harrison, 2003). Primary particles related to traffic 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 are minor contributors to UFP loading in urban environments (Buonanno and Morawska 2015). Nucleation mode particles related to traffic are formed behind the exhaust tailpipe as the exhaust gases are diluted and cooled with ambient air (Charron and Harrison, 2003). The most crucial aspect of particle formation behind the exhaust tailpipe is the three-dimensional representation of the dilution pattern, which involves varying length and time scales (Zhu et al., 2002; Uhrner et al., 2007; Wehner et al., 2009; Huang et al., 2014). Strictly speaking, these particles are secondary, but as they form so close to source, most works regard them as primary.

Additionally, new particle formation of regional origin (Kulmala et al., 2004; Wehner et al., 2007; Costabile et al., 2009) has also been detected in urban areas. This in contrast to what was assumed in the past, which is 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 (Wiedensohler et al., 2002). This is usually attributed to the fact that such natural environments are characterised by 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 originally demonstrated in Atlanta, USA (Woo et al., 2001), Birmingham, UK (Alam et al., 2003) and Pittsburgh, USA (Stanier et al., 2004), and subsequently in many cities worldwide (Pey et al., 2008, 2009; Wu et al., 2008; Costabile et al., 2009; Rimnácová et al., 2011; Salma et al., 2011; Dall'Osto et al., 2013; Betha et al., 2013; Cheung et al., 2013; Brines et al., 2014).

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 Northern Europe, nucleation events in many urban areas are 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 likely to be the higher intensity of solar radiation in the Southern European areas, and/or possible site specific chemical precursors.

In this regard it is worth remembering that UFP and Black Carbon (BC - primary traffic particles emitted from incomplete combustion) often share the same combustion-related emission sources in urban environments (Peters et al., 2014; Ruths et al., 2014). In other words, different pollutant metrics are being evaluated to accurately characterise traffic related particle emissions in urban areas. However, whilst the combination of particle number and black carbon concentrations might be a promising approach to assess the spatio-temporal behaviour of traffic related particle concentrations (Dall'Osto et al., 2013, Ruths et al., 2014), Reche et al. (2011) clearly show that particle number concentration alone is not sufficient to accurately demonstrate a traffic related emission, since high number concentrations of particles can also be associated with new particle formation events. Recently, Dall´Osto et al. (2013) demonstrated the complexity of the evolution of traffic particles and the different types of nucleation events occurring in the Mediterranean basin.

Hence, 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. Reche et al. (2011) demonstrated that with aerosol number concentration (PN) and BC concentration measurements, useful information can be drawn on the differences in primary emissions and nucleation enhancements across European cities. The present work considers not only PN, but also aerosol size distribution. This is one of the most important properties of particles, which helps in understanding aerosol dynamics, as well as determining their sources (Harrison et al., 2011; Salimi et al., 2014; Beddows et al., 2015). In the present work, size-resolved particle number concentration measurements using a Scanning Mobility Particle Sizer, (SMPS, see Table S2 for details) sampled in a number of urban areas are presented and discussed. The complexity of the data is further reduced by applying *k*-Means clustering analysis (Beddows at al., 2009; Dall'Osto et al., 2011b and 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). Salimi et al. (2014) showed that the *k*-Means clustering technique was found to be the preferred one among several used, and Väänänen et al. (2013) showed that clustering analysis is a good tool for studying aerosol dynamics and new particle formation events. In other words, we use a wide aerosol size distribution (10.2-17.5/101.8-615.3nm) and not only the total particle number concentrations to assess the source of ultrafine particles in the urban atmosphere, leading to a better apportionment. The identification of the main pollution sources contributing to ultrafine particles affecting urban environments enables quantitative estimation of the temporal prevalence of each source.

Our main databases are taken from two cities in Southern Europe (Barcelona and Madrid, Spain) and one in Eastern Australia (Brisbane). To complement the study, two additional datasets from high insolation areas (also located in temperate climatic areas) are analysed: two years of data from a regional background site regularly impacted by the Rome (Italy) pollution plume and three months of data from an urban background site in Los Angeles (USA).

2 Methodology

2.1 Site locations

Following previous work (Reche et al., 2011; Kumar et al, 2014) we selected four cities (Barcelona, Madrid, Rome and Los Angeles), all 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 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:

1) Barcelona (BCN), Spain: located on the north-western Mediterranean basin it has 1.7 million inhabitants although the metropolitan area exceeds 4 million. The SMPS sampling site (Palau Reial) can be 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).

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 was 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.

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).

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.

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. The monitoring sites in the cities of Barcelona, Madrid, Brisbane and Los Angeles were classified as urban background, whereas the one in Rome was further away from the city. Regarding Los Angeles only three months of measurements were available, which was not sufficient for studying the annual trends. However, we believe the sites of Rome and Los Angeles add some important supporting information to further validate our findings.

2.2 Measurements

2.2.1 Particle number size distributions

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. Although the use of aerosol drier is advisable (Swietlicki at al., 2008; Colbeck et al., 2014), it was not possible at the time of sampling. Nevertheless, data were thoroughly checked to avoid possible humidity influences (Costabile et al., 2010) 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.

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., 2011b; 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. As recently discussed in Hussein et al. (2014), it is not prudent to describe the size distributions with either too few or too many clusters. Few clusters (2-4) are not enough to explain variations and detailed differences in the particle number size distributions observed in the urban atmosphere. However, using too many (>10) clusters often makes the aerosol source attribution more challenging. It is important to note that the different aerosol size distribution clusters were merged not only upon their similar size distributions among each other but also by considering strong correlations with other physical and chemical parameters obtained with other instruments (Beddows et al., 2009; Dall'Osto et al., 2011a). Additionally, the reduction to three more-generic classifications, while not based on statistics, is based on existing knowledge of distributions typically observed and associated with these categories. The average aerosol size distributions of the three aerosol categories (obtained by averaging the SMPS clusters of each individual category) are presented in Fig. 3. 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 three main categories: “Traffic”, “Nucleation” and “Background pollution and Specific cases”. 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 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. Results from Rome and Los Angeles are herein used only to complement the discussion, given their limitations (site location and limited data availability, respectively).

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 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.

- 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. The evolution of these aerosol size distribution modes attributed to traffic have already been widely discussed in previous studies (Dall´Osto et al., 2011; Dall´Osto et al., 2012; Brines et al., 2014).

- 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). 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. As recently discussed in Kumar et al. (2014), the volatile nature of the traffic nucleation mode particles raises issues in relation to their reliable measurement and may also enhance their spatio-temporal variability following their emission into the atmospheric environment (Dall'Osto et al., 2011b). A traffic- related cluster peaking during noontime was also related to the extension of the morning traffic peak, which is similar to the diurnal variation of NO_x (Liu et al., 2014). The pattern of this factor is similar to the local traffic factor found in Beijing in previous study (Wang et al.,2013a).

3.1.2 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 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. NU is observed at midday or early afternoon more intensely during spring and summer (see Fig. S1b). This cluster is generally characterised by very high solar irradiance, high wind speed and low concentration of traffic pollutants (see Fig. S2). 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.

3.1.3 Background pollution and Specific cases clusters

- Urban Background (UB): the Urban Background cluster can be observed at all three 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.

- 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 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 Supporting *k*-Means cluster results from 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 (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).

3.3 *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). The closer nodes represent similar clusters, although not sufficiently alike to form a new cluster. Conversely, the more distant nodes represent the most dissimilar clusters. 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 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.

4 Discussion

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

- Background pollution and Specific cases. 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. The Urban Background cluster usually describes the cleanest conditions encountered at the urban sites, ranging from 6 to 22% of the time (see Table S4). The resulting average spectra for all Urban 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 cases were 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 S4). The difference in 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.

- 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., 2011b). This is the dominant category at all sites, showing the high prevalence of traffic emissions in the ultrafine PN 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).

- Nucleation events. Nucleation events accounted 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). 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 minor peak can be observed around 3 p.m., when the nucleated particles downwind of Rome reach the sampling site.

Whilst the occurrence of an increase in PN levels related to photochemical nucleation events at midday was previously discussed (Reche et al. 2011), this study allows study of how new particle formation events evolve in the urban areas studied. Figure 5 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). 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.

Although only three months of data are available, the same conclusion can be extracted from the urban Los Angeles site, whereas aged nucleated particles downwind of Rome (20-40 nm) reach the Rome regional site in the early afternoon (Fig 5d-e). Figure 6 shows aerosol size distribution data collected in Barcelona, Madrid and Brisbane during the days when nucleation events were detected (as *k*-Means cluster NU). Additionally, temperature,

relativity humidity, solar radiation and nitrogen oxide gaseous concentrations are plotted. A clear burst of particles can be seen at midday when gaseous pollutants are diluted and maximum insolation occurs.

It is worthy of note that weekday/weekend ratios were calculated for each cluster at each city in order to analyse the impact of traffic/urban emissions on the clusters occurrence. The highest average ratio (1.3) was found for the T1 cluster, strengthening its relation to fresh traffic emissions. On the other hand, T2 and T3 clusters average ratio was 1-1.1, indicating relative independence on fresh traffic emissions, in contrast to T1. The nucleation cluster was found to occur more often during weekends (average ratio 0.9). The lowest ratio was recorded for the UB cluster during weekends (average ratio 0.7) reflecting its background nature.

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 particle condensation sink due to traffic emissions might constrain the growth of nucleated particles. Instead, nucleation events consist of 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.

5 Implications and Conclusions

This study shows that traffic is a main source of UFP in the urban atmosphere, accounting for 44-63% of the time. The quantified particle number concentration contribution of motor vehicle emissions was also the major source in other urban locations: 47.9% in Beijing (Liu et al., 2014), 69% in Barcelona (Pey et al., 2009; Dall´Osto et al., 2012), 65% in London (Harrison et al., 2011; Beddows et al., 2015), 69% in Helsinki (Wegner et al., 2012), 42% in Pittsburgh and 45% in Rochester (Woo et al., 2001; Stanier et al.,2004). Recent source contributions of ultrafine particles in the Eastern United States also identified gasoline automobiles being responsible for 40% of the ultrafine particle number emissions, followed by industrial sources (33%), non-road diesel (16%), on-road diesel (10%), and 1% from biomass burning and dust (Posner and Pandis, 2015). Vehicle emissions consist of hot gases and primary particles, which are a highly dynamic and reactive in nature mixture (Kumar et al., 2011), resulting in rapid physical and chemical transformations of the emitted particles following atmospheric dilution and coolong. There is a need for more field studies to map traffic related particle number concentrations and to understand the particle dynamics and their dispersion in urban areas (Goel and Kumar, 2014).

However, the second major source of ultrafine particles in the urban atmosphere of the developed urban areas herein presented is secondary aerosol formation. It is important to remember that nucleation events in Northern European urban areas are found to be infrequent. In the Helsinki urban atmosphere they are usually observed during noon hours with a maximum during spring and autumn (Hussein et al., 2008), and overall representing only about 2% of the time (Wegner et al., 2012). Additionally, these events were regional because they were observed at Hyytiälä (250 km north of Helsinki). By contrast, in Southern Europe, Reche et al. (2011) showed that new particle formation events do occur more frequently than in Northern Europe. However, only PN was reported in that study, making it harder to link aerosol sources and processes. Nonetheless, this study clearly showed how new particle formation events impact the urban areas studied. In order to discuss this further, we link our discussion to that reported in Dall´Osto et al. (2013). At least two main different main types of new particle formation event can be seen in the Mediterranean urban environment:

(1) A regional type event, originating over 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, as clearly shown in Fig. 6.

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) as they are often followed by particle growth showing a banana-shape (Cheung et al., 2011). This may be due to the fact that the Brisbane site is located in a relatively clean environment. By contrast we find that the majority of new 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 (Figure 5, 6), as reported in Dall´Osto et al. (2013).

It should be noted that many urban areas exposed to high insolation are also characterised by high condensation sinks. This is the case of many developing urban areas, where new particle formation events are limited. For example, particle bursts in the nucleation mode size range (5-25 nm), followed by a sustained growth in size were observed very rarely (only 5 out of 79 observation days) in a tropical Southern India site, less frequently than at most other locations around the world during May-July (Kanawade et al., 2014a). New particle formation at two distinct Indian sub-continental urban locations were observed with lower frequency at Kampur (14%) than that at Pune (26%), due to the presence of pre-existing large particles at the former site (Kanawade et al., 2014b). Observations of new aerosol particle formation in a tropical urban atmosphere (Betha et al., 2013) were also found to be suppressed by very high pre-existing particle concentrations during haze periods (Betha et al., 2014). Zhu et al. (2014) reported fewer new particle formation events in a severely polluted atmosphere (Qingdao, China) than in Toronto (Canada). Long-term measurements of particle number size distributions in urban Beijing and in the North China Plain showed homogeneous nucleation events

characterized by the co-existence of a stronger source of precursor gases and a higher condensational sink of pre-existing aerosol particles than European cities (Wang et al., 2013a, b).

Regional nucleation can be seen in urban areas more frequently over the weekend (Sabaliauskas et al., 2013). Ragettli et al. (2014) recently reported spatio-temporal variation of urban ultrafine particle number concentrations, showing that the most important predictor for all models was the suburban background UFP concentration, explaining 50% and 38% of the variability of the median and mean, respectively. Frequencies of new particle formation (NPF) events in China were much higher at urban and regional sites than at coastal sites and during open ocean cruise measurement (Peng et al., 2014).

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 stages 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. The urban nucleation events described in this paper presumably have an anthropogenic origin, or at least are 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). On average, nucleation events lasting for two hours or more were detected in 55% of the days, this extending to over four hours in 28% of the days, demonstrating that the atmospheric conditions in urban environments do not favour photochemically nucleated particle growth. Traffic remains a major source of

ultrafine particles in the urban atmosphere, and regional new particle formation can impact urban areas. However, peaks of ultrafine particle number concentrations at midday (Reche et al., 2011), due to localised urban nucleation occurring in the city (Dall´Osto et al., 2013), and seen also in a number of other urban areas as reported in Figure 5 of this work, suggest it is an important phenomenon (occurring on average 16% of the time), and should be taking into account in the design and implementation of air quality monitoring networks (Duyzer et al., 2015).

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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.

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

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.

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 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.

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.

Figure 4: Average aerosol size distributions for the main *k*-Means cluster category: Traffic, Nucleation and Urban Background. 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.

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.

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 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%)
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%)
Background pollution and Specific case (SC)	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%)	-
	Nitrate (NIT)	36±1 nm (100%)	63±1 nm (100%)	-
	Growth 1 (G1)	-	-	28±1 nm (100%)
	Growth 2 (G2)	-	-	37±1 nm (100%)

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

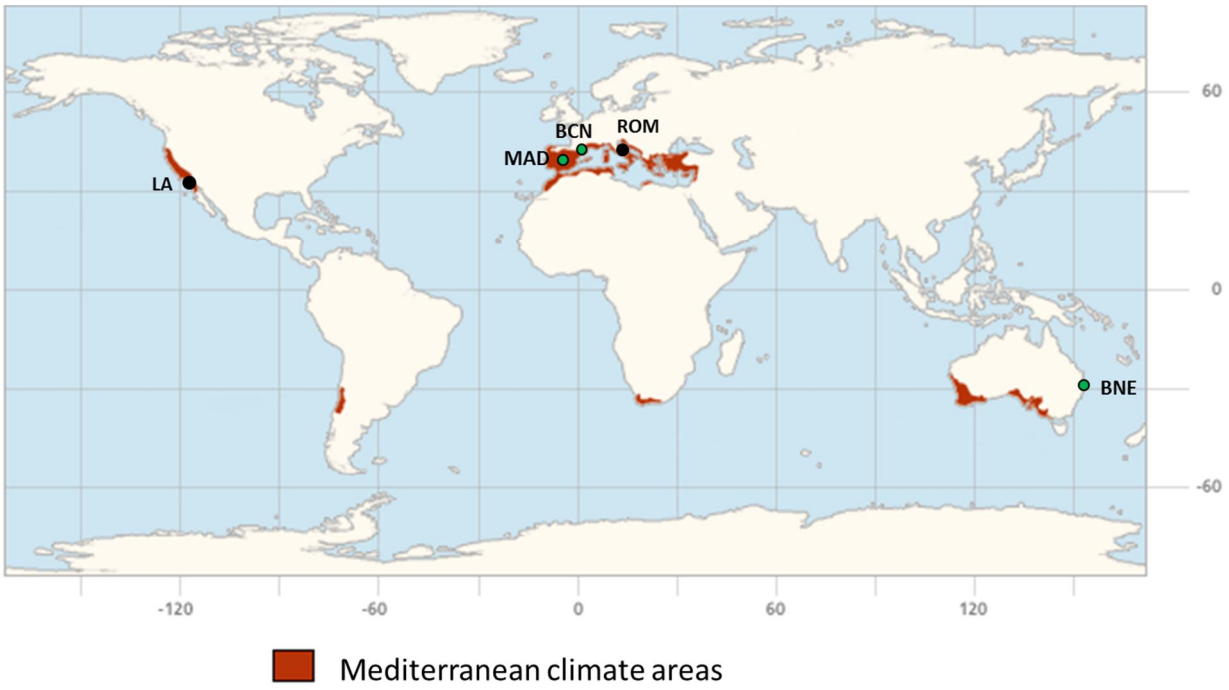
Category	Barcelona	Madrid	Brisbane
Traffic	63%	58%	44%
Nucleation	15%	19%	14%
Background and SC	22%	23%	42%
	100%	100%	100%

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.

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

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%



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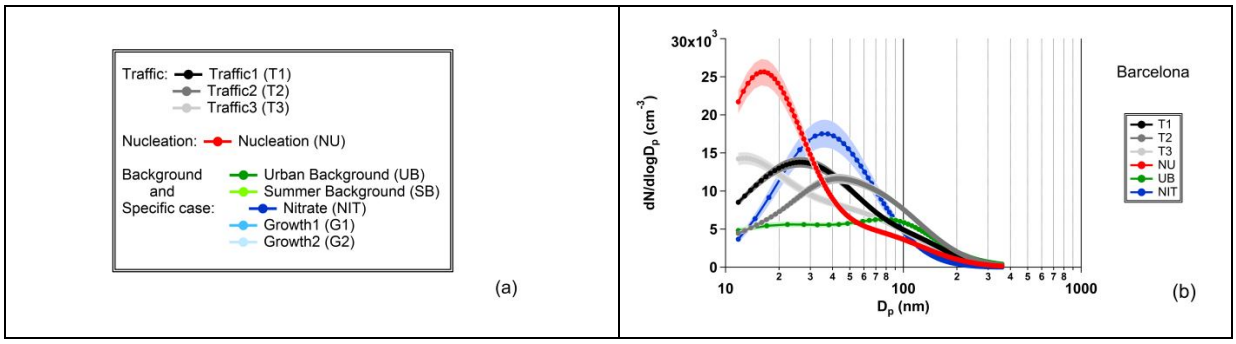

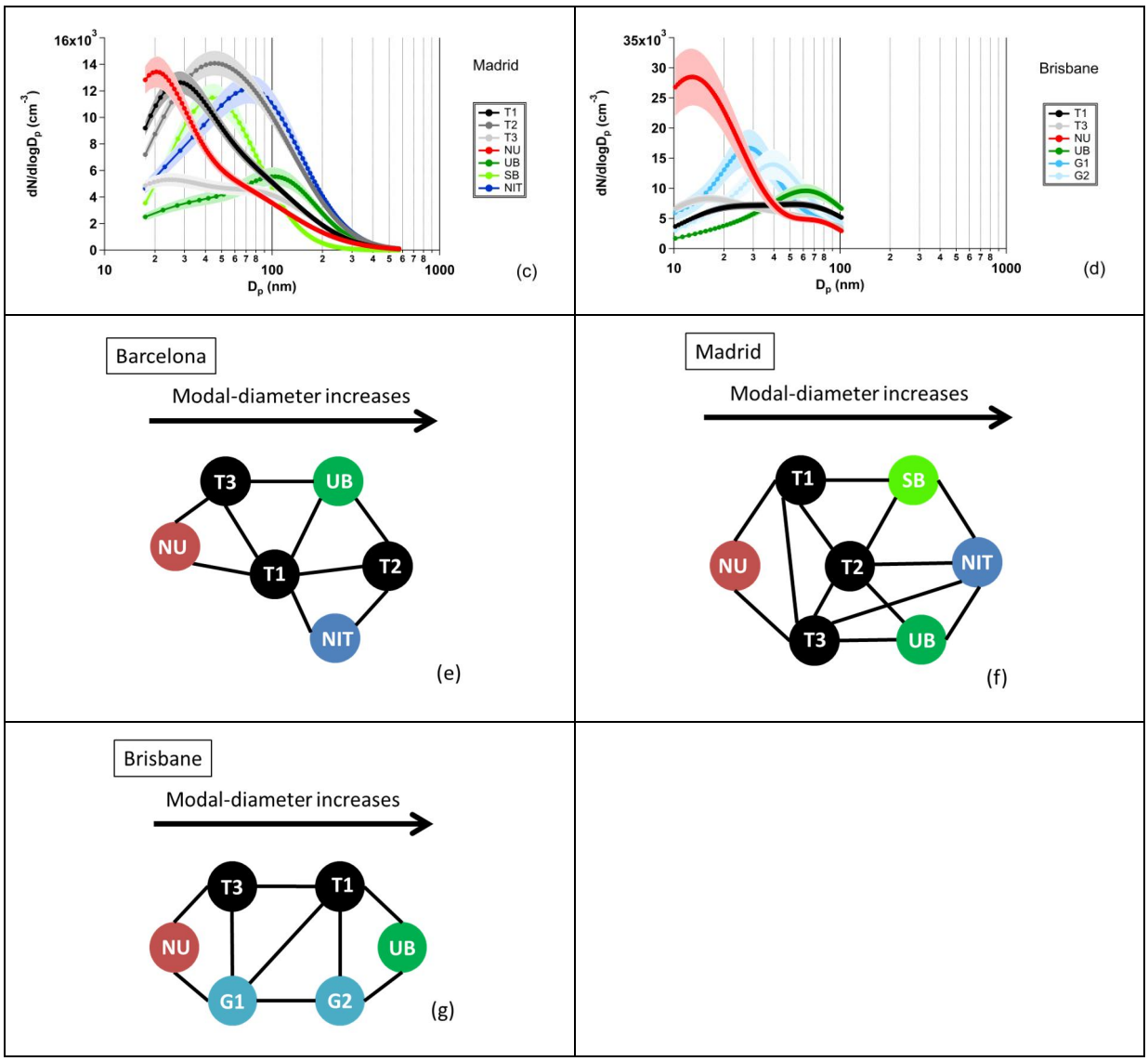

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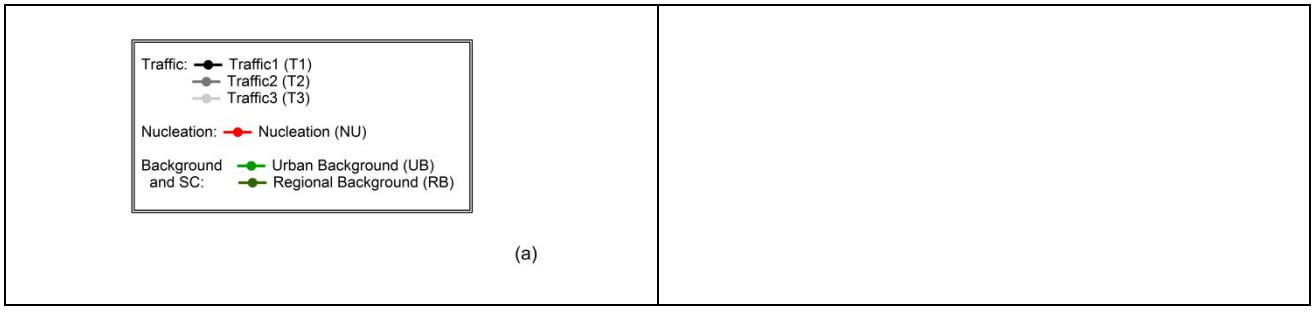

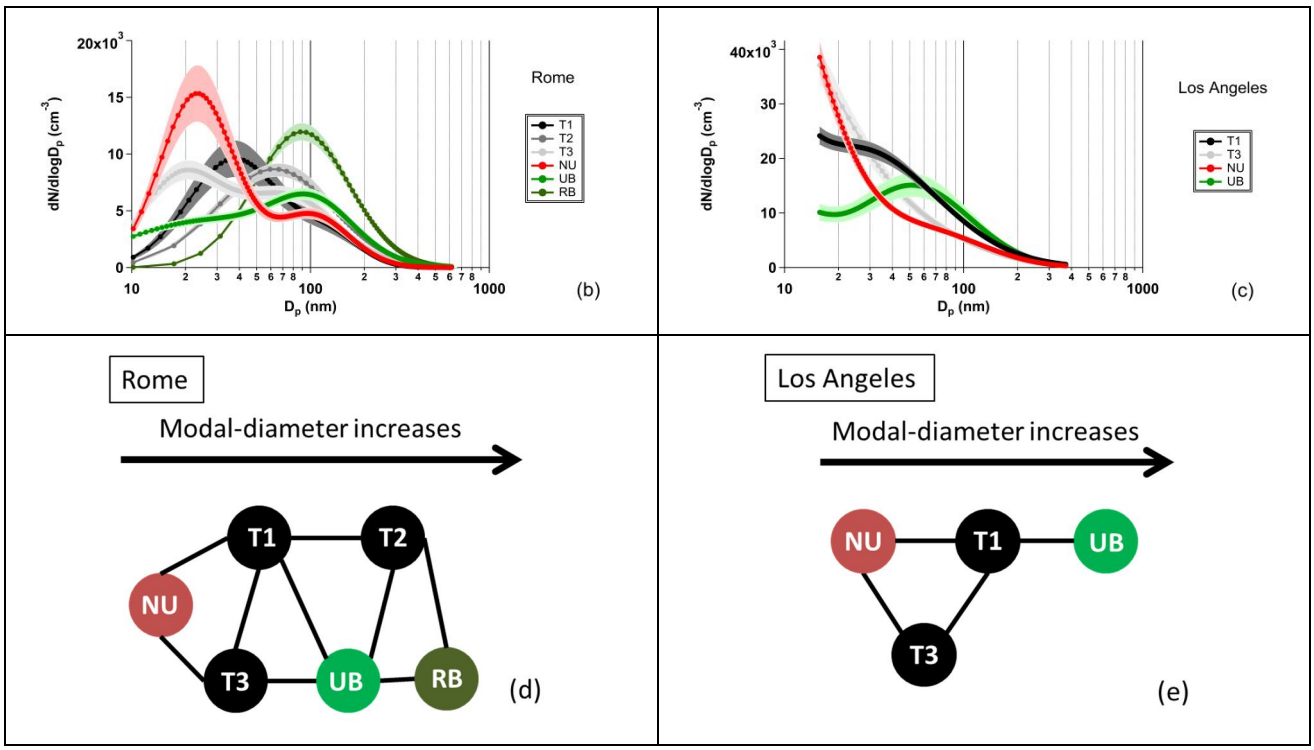

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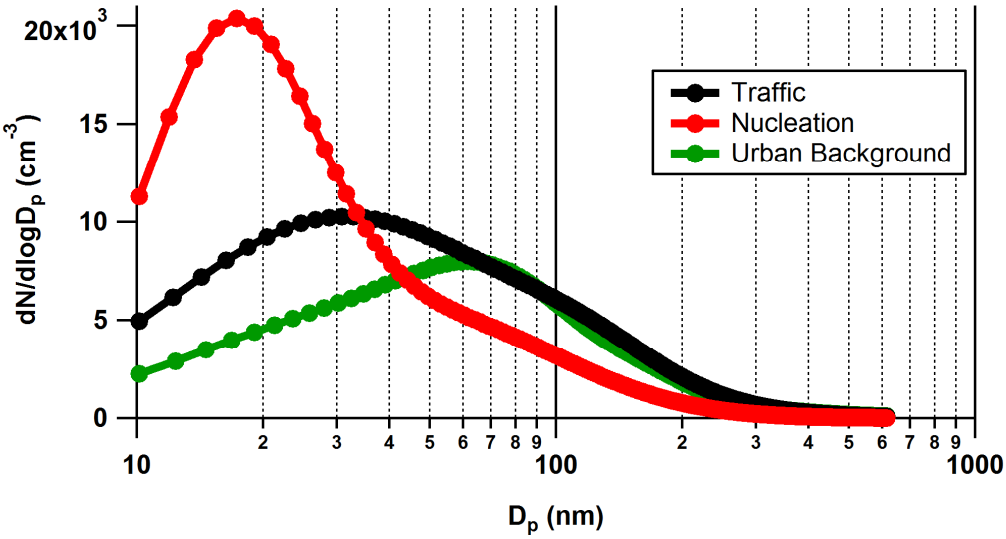

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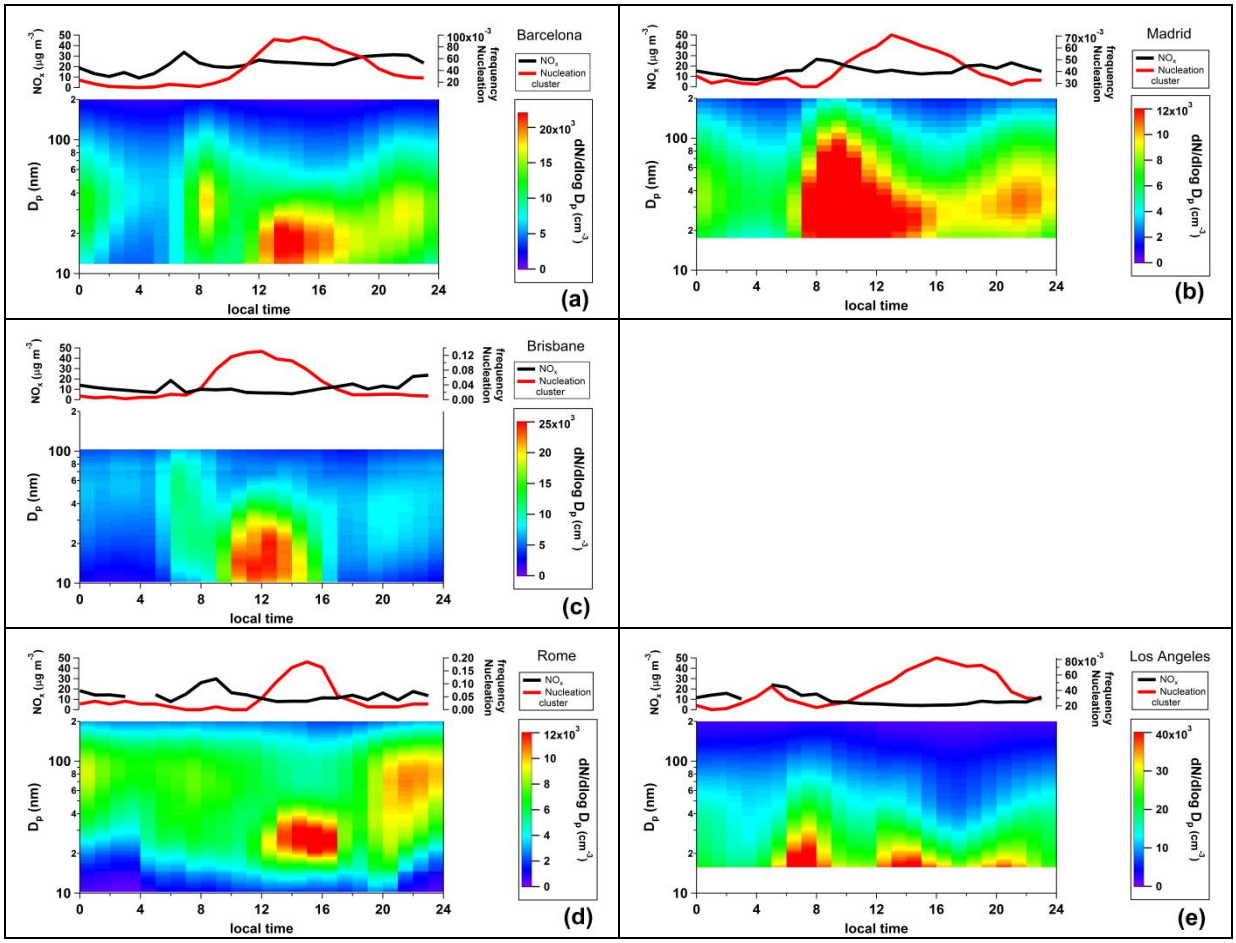

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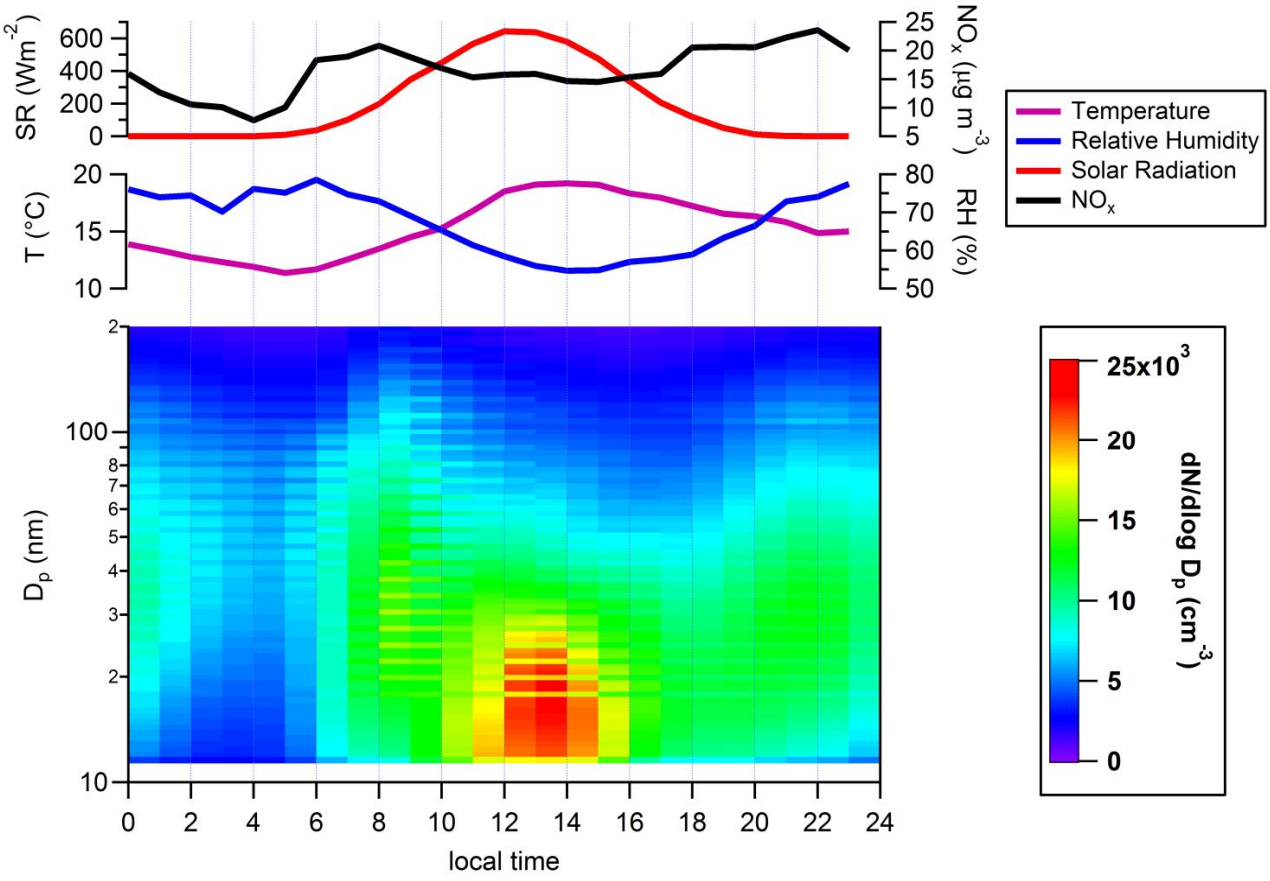

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