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Frequency of new particle formation events in the urban Mediterranean climate

M. Brines[1,2], **M. Dall'Osto**[3,4], **D. C. S. Beddows**[4], **R. M. Harrison**[4,5], **F. Gómez-Moreno**[6], **L. Núñez**[6], **B. Artíñano**[6], **F. Costabile**[7], **G. P. Gobbi**[7], **F. Salimi**[8], **L. Morawska**[8], **C. Sioutas**[9], and **X. Querol**[1]

[1]Institute of Environmental Assessment and Water Research (IDÆA) Consejo Superior de Investigaciones Científicas (CSIC), C/Jordi Girona 18–26, 08034 Barcelona, Spain
[2]Department of Astronomy and Meteorology, Faculty of Physics, University of Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain
[3]Institute of Marine Sciences (ICM) Consejo Superior de Investigaciones Científicas (CSIC), Pg. Marítim de la Barceloneta 37–49, 08003 Barcelona, Spain
[4]National Centre for Atmospheric Science Division of Environmental Health & Risk Management School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
[5]Department of Environmental Sciences/Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah, 21589, Saudi Arabia
[6]CIEMAT, Environment Department, Unidad Asociada CSIC-CIEMAT, Av. Complutense 40, 28040 Madrid, Spain
[7]CNR – Institute for Atmospheric Sciences and Climate, via Fosso del Cavaliere, 100, Rome, Italy

[8]International Laboratory of Air Quality and Health, Queensland University of Technology, G.P.O. Box 2434, Brisbane QLD 4001, Australia
[9]University of Southern California, Sonny Astani Department of Civil and Environmental Engineering, 3620 S Vermont Ave., Los Angeles, CA, 90089, USA

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Correspondence to: M. Brines (mariola.brines@idaea.csic.es)

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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 have shown that – in southern European urban regions at least – new particle formation events can also contribute to UFP. In order to quantify such events we systematically studied four cities with a Mediterranean climate: Barcelona, Madrid, Rome and Los Angeles. The city of Brisbane is also included in our study due to its similar climate. Five long term datasets (from 3 months to 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 41–63 % of the time), "Background Pollution" (6–53 %), "Nucleation" (6–33 %) and "Specific case" (7–20 %) the latter being site specific. 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 new particle formation events. This work shows that the average occurrence of particle size spectra dominated by new particle formation events was 18 % of the time, showing the importance of this process as a source of UFP in the Mediterranean urban atmosphere. 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 Mediterranean urban environments.

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

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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) or as carbonaceous soot agglomerates formed by fuel combustion (Kittelson, 1998). 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.

It has been often assumed that photonucleation events only occur in background and regional environments such as clean coastal environments (O'Dowd et al., 2010), forest areas (Boy and Kulmala, 2002), semi-clean savannah environments (Vakkari et al., 2011), high altitude locations (Sellegri et al., 2010) and regional background environments (Laaksonen et al., 2005). 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. Therefore, a lower frequency of nucleation events is usually expected. Nevertheless, there are studies showing that these events can be detected in urban areas. The first studies of this type were recorded in Atlanta, USA (Woo et al., 2001), Birmingham, UK (Alam et al., 2003) and Pittsburg, USA (Stanier et al., 2004). Since then, many studies in cities worldwide have supported such scenarios (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., 2012; 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). They are characterised by a high increase in particle number concentrations (PN) in the nucleation mode and, if conditions are favourable, subsequent particle growth in the following hours. 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)

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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 Mediterranean climate areas. 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 urban Mediterranean climate environments. To this end a number of cities have been selected. Three of the cities are located in Europe (Barcelona, Madrid and Rome), one is located in Australia (Brisbane) and one in the south-western USA (Los Angeles). Although the city of Brisbane is not located in a Mediterranean climate area, its humid subtropical climate presents many similarities to it and so Brisbane was included in the present study.

Size-resolved particle number concentration measurements using the 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).

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2 Methodology

2.1 Mediterranean climate and site locations

The Mediterranean climate is categorised as *dry-summer subtropical* 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 W m^{-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 Fig. 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. Finally, the city of Brisbane (Australia) was also included. Although its climate is categorised as *humid subtropical* due to the higher mean annual rainfall (1150 vs. 600 mm for the Mediterranean climate), it has been included in the study given the many climatological similarities. Both areas share mild winters and warm summers with prevalent sunny days. A detailed description of the five selected cities follows:

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 the Diagonal Avenue (90 000 vehicles per working day), which is primarily used by commuters (see Table S1). Previous work in the study area reflected 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 plume is fed mainly from traffic emissions, as it is a dry port and relevant crossroad. 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.

3. 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 being considered as a regional background, it is regularly impacted by pollutants transported from the area of Rome, due to the sea-breeze circulation. 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).

4. 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.

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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 contribution 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 work in the study area (Hudda et al., 2010) analysed SMPS data sampled at this site in a multisite study carried out in 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 attributed to secondary photochemical particle formation.

2.2 Measurements

2.2.1 Particle size distribution number concentrations

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, Los Angeles, Brisbane, and Madrid were classified as urban background, whereas the one in Rome was further away from the city. The SMPS low-cut point ranged from 10.2 to 17.5 nm whereas the SMPS high-cut point varied from 101.8 to 615.3 nm. 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; Rome: Costabile et al., 2010; Brisbane: Cheung et al., 2011; Los Angeles: Hudda et al., 2010). Due to the different time resolution of each instrument, all measurements were averaged to 1 h 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 h resolution to match the SMPS measurements.

2.3 Data analysis (*k*-Means)

The large amount of data presented in this work (31 448 h 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.

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 Fig. 2). 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

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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 Fig. 2). To further simplify the results, the clusters have been thoroughly divided in four main categories: "Traffic", "Background Pollution", "Nucleation" and "Specific case". Detailed features of each *k*-Means size distributions can be found in Tables 1 and S4 and Fig. 2. Finally, it is important to remember that the clustering results can provide a much higher amount of information that the one presented here. Nevertheless, the objective of this study is to present four main aerosol size distribution categories in order to quantify the impact of new particle formation event in the urban Mediterranean atmosphere.

3.1.1 Traffic-related clusters

- Traffic 1 (T1): this cluster can be seen at all monitoring sites, occurring 7–36 % 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 nucleation mode) and another at 70–130 nm (soot mode) (see Table 1). 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 Figs. 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, Madrid and Rome, occurring 22–27 % of the time (Table S4). It shows a bimodal size distribution with a minor peak at 20–40 nm and a dominant one at 60–90 nm (see Table 1). It is usually observed during the evening and night, and contains high concentration of traffic pollutants,

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like T1 (see Figs. 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 Fig. 2.

- Traffic 3 (T3): this traffic related cluster was found in all the monitored cities 7–25 % 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 50–80 nm (see Table 1). 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, Rome and Brisbane (see Fig. 2b–e) (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 distributions modes simultaneously detected at four monitoring sites during SAPUSS were reported.

3.1.2 Background pollution clusters

- Urban Background (UB): the Urban Background cluster can be observed at all sites 6–25 % of the time (see Table S4). The size distributions present a bimodal peak at 20–40 nm and at 70–120 nm (see Table 1). At Barcelona, Madrid and Los Angeles – cities highly influenced by road traffic emissions – the dominant peak is the finest one, whereas in Brisbane and Rome the larger peak prevails (see Table 1). Urban background clusters were usually observed during the night time, associated with relatively clean atmospheric conditions in the urban environment (see Figs. 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

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44 ± 1 nm (see Table 1). It is seen during the summer nights and thus influenced by low levels of traffic pollutants, pointing towards clean summer atmospheric conditions.

- 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 Sect. 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).

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 Mediterranean urban environments (see Table S4). It occurs for between 6 and 33 % of the measured periods and has a dominant nucleation mode peak in the range 10–25 nm and a minor size peak in the Aitken mode at 50–100 nm (see Table 1), 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 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

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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 Sect. 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 (Fig. 3). 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 3 shows the 5 corresponding CPDs for the 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 1). 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, SB, RB), 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. Madrid and Rome (Fig. 3b and c, respectively) show site specific background clusters. The SB cluster in Madrid is loaded with traffic particles from T1 and T2 before it contributes to the Nitrate (NIT) cluster. Nevertheless, the regional nature of the monitoring site in Rome is reflected in the RB cluster, located at the far right end of the CPD. Other site specific clusters such as Nitrate (NIT) are only observed in Barcelona and Madrid (Fig. 3a and b, 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 1). The remaining Growth clusters in Brisbane (G1 and G2) are positioned in the centre of the CPD (Fig. 3d) 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 Sect. 3.1 can be summarised and simplified in the following categories:

- Traffic. It 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 except for Rome (site located outside the city), 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 41 % in Rome to 63 % in Barcelona (see Table 2).

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The average Traffic size distribution shows a minor peak in the nucleation mode at 20 ± 1 nm and a main one in the Aitken mode at 44 ± 4 nm (see Fig. 4 and Table 3). According to vehicle emission studies, the finest mode corresponds with nucleation mode 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 6 to 53 % of the time (see Table 2). The resulting average spectra for all background clusters (Fig. 4) shows a bimodal size distribution, with a dominant peak in the Aitken mode at 80 ± 40 nm, reflecting aged aerosols of an anthropogenic origin, and a minor peak at 24 ± 40 nm (see Table 3).

– 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 seen only in Brisbane. Each cluster represents around 10 % of the time at their respective sites (see Table 2). 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 Fig. 3). The Growth clusters reflect the size mode increase of nucleation particles due to subsequent growth (see Table 1), since they are recorded after nucleation episodes.

– Nucleation events. Nucleation events account for 6–33 % of the hourly observations, with an average of 18 % of the time, indicating nucleation as an important source of UFP in Mediterranean climate urban areas (see Table 2). 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. The average Nucleation size distribution (Fig. 4) is characterised by a high PN nucleation mode peak at 19 ± 1 nm and a lower PN peak in the Aitken mode at 41±7 nm (Table 3). 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 (9970 ± 100 cm^{-3}) of all categories (see Fig. 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 Mediterranean areas, as it is the dominant particle number concentration source on average for 18 % 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 (Fig. 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 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

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worldwide cities sharing a Mediterranean climate. Furthermore, this study shows that new particle formation events in the urban Mediterranean environment often fail to grow to sizes larger than 30–40 nm. 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 city of Brisbane exhibits new particle formation events starting in the morning (see Fig. 5d), 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 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 (20–100 nm 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, Rome and Brisbane size distributions (Figs. 5 and 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

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in solar radiation intensity and the prevalence of traffic emitted particles in the evening. Little is known about health effects of UFP in urban areas (HEI Overview Panel, 2013) or about the mechanisms and chemical components responsible for such events. Additionally, the health effects of the two nucleation event types discussed herein are not known. However, our results suggest that urban nucleation has a likely anthropogenic origin, or at least is influenced by anthropogenic precursors. This is due to the fact that those 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.

5 Conclusions

With the aim of evaluating the nature and impact of urban nucleation events on levels of ambient UFP in Mediterranean climate cities, we apply a unified specialized tool to long term data sets (3 months to 2 years) sampled at several Mediterranean urban environments. Size resolved particle measurements were performed in four urban background environments with a Mediterranean climate: Barcelona, Madrid, Rome and Los Angeles. The Australian city of Brisbane was also included due to its climatic similarities. Individual studies have evidenced 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 41–63 % of the time), nucleation events accounted on average for 18 % of the observations. This is reflected in the midday peak of daily average PN levels recorded at many of the study cities due to nucleation. Most of the new particle formation events were not followed by growth. In other words, most

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of the detected events lasted about 1–4 h, 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 about 1–4 p.m. (Dall'Osto et al., 2013). Both events did not last more than 3–6 h, indicating the urban environment is not one that allows full growth of particles as seen in more remote regional backgrounds. Nevertheless, it remains an important source of UFP in the urban Mediterranean atmosphere.

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Table 1. Log-Normal fitting peaks for each cluster category *k*-Means size distribution at each site and the corresponding peak area percentage.

Category	Subcategory	Barcelona	Madrid	Rome	Brisbane	Los Angeles
Traffic	Traffic 1 (T1)	26 ± 1 nm (84 %), 130±4 nm (16 %)	25 ± 1 nm (31 %), 70 ± 6 nm (69 %)	37 ± 1 nm (65 %), 130±7 nm (35 %)	21 ± 1 nm (30 %), 77 ± 1 nm (70 %)	21 ± 1 nm (100 %)
	Traffic 2 (T2)	23 ± 2 nm (31 %), 36 ± 1 nm (8 %), 75 ± 2 nm (61 %)	31 ± 3 nm (30 %), 83 ± 9 nm (70 %)	59 ± 2 nm (91 %), 102 ± 8 nm (9 %)	–	–
	Traffic 3 (T3)	11 ± 1 nm (21 %), 48 ± 1 nm (79 %)	21 ± 1 nm (24 %), 92 ± 3 nm (76 %)	19 ± 1 nm (20 %), 75 ± 1 nm (80 %)	14 ± 1 nm (18 %), 52 ± 4 nm (82 %)	< 15 nm (73 %), 66 ± 1 nm (27 %)
Background	Urban Background (UB)	22 ± 1 nm (61 %), 96 ± 1 nm (39 %)	40 ± 1 nm (53 %), 119±1 nm (47 %)	27 ± 2 nm (46 %), 105±1 nm (54 %)	63±2 nm (100 %)	45 ± 1 nm (100 %)
	Summer Background (SB)	–	44±1 nm (100 %)	–	–	–
	Regional Background (RB)	–	–	89±1 nm (100 %)	–	–
Nucleation	Nucleation (NU)	16 ± 1 nm (53 %), 69 ± 2 nm (47 %)	19 ± 1 nm (24 %), 48 ± 2 nm (76 %)	23 ± 1 nm (43 %), 102±2 nm (57 %)	13 ± 1 nm (74 %), 77 ± 1 nm (26 %)	< 15 nm (62 %), 67 ± 3 nm (38 %)
Specific case (SC)	Nitrate (NIT)	36±1 nm (100 %)	63±1 nm (100 %)	–	–	–
	Growth 1 (G1)	–	–	–	28±1 nm (100 %)	–
	Growth 2 (G2)	–	–	–	37±1 nm (100 %)	–

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Table 2. Cluster categories (Traffic, Background, Nucleation and Specific case (SC)) and their occurrence at each site.

Category	Barcelona	Madrid	Rome	Brisbane	Los Angeles
Traffic	63 %	58 %	41 %	44 %	61 %
Background	15 %	13 %	53 %	22 %	6 %
Nucleation	15 %	19 %	6 %	14 %	33 %
SC: Nitrate	7 %	10 %	–	–	–
SC: Growth	–	–	–	20 %	–
	100 %	100 %	100 %	100 %	100 %

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Table 3. *k*-Means cluster categories average size distribution size mode peaks and corresponding area percentage.

Category	nucleation	Aitken	accumulation
Traffic	20 ± 1 nm (8 %)	44 ± 4 nm (92 %)	–
Background	24 ± 40 nm (10 %)	80 ± 40 nm (90 %)	–
Nucleation	19 ± 1 nm (21 %)	41 ± 7 nm (79 %)	–

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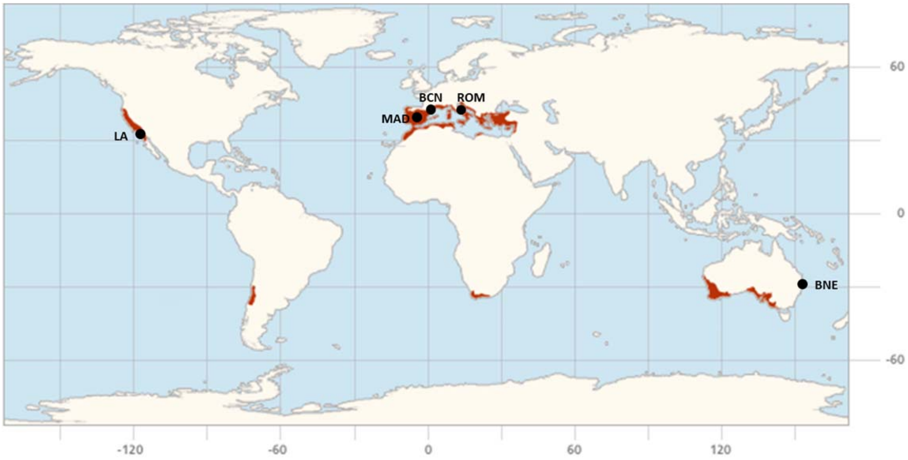

Figure 1. Location of the 5 cities selected for the study: Los Angeles (LA), Madrid (MAD), Barcelona (BCN), Rome (ROM) and Brisbane (BNE).

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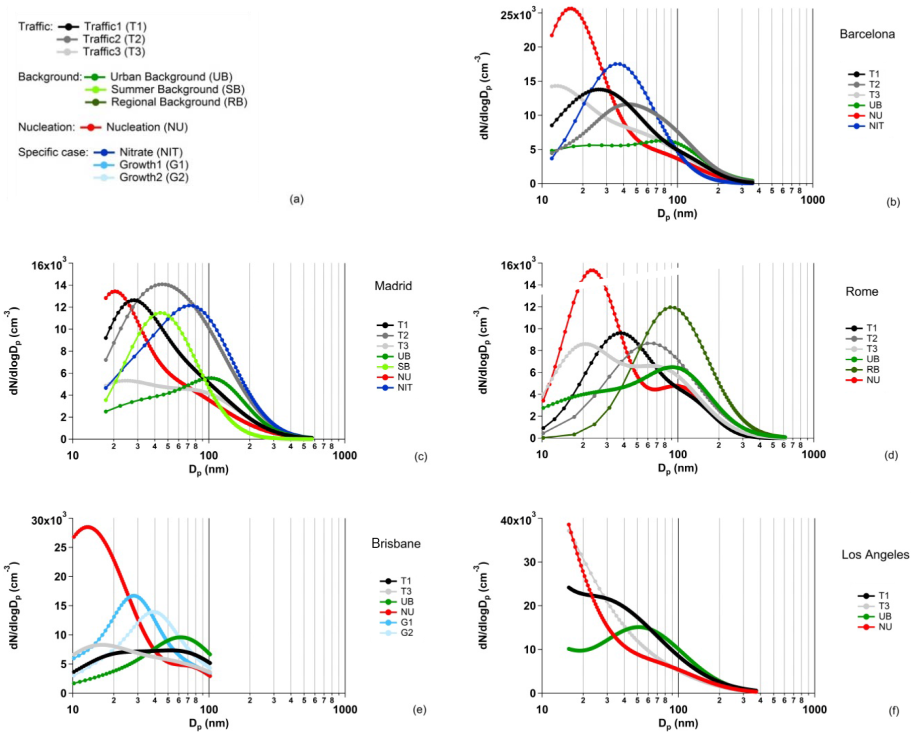

Figure 2. Aerosol size distribution results of the *k*-Means cluster analysis performed on the SMPS data at each selected city: **(a)** legend, **(b)** Barcelona, **(c)** Madrid, **(d)** Rome, **(e)** Brisbane, **(f)** Los Angeles. Please note the different scales for dN/dlogD$_p$.

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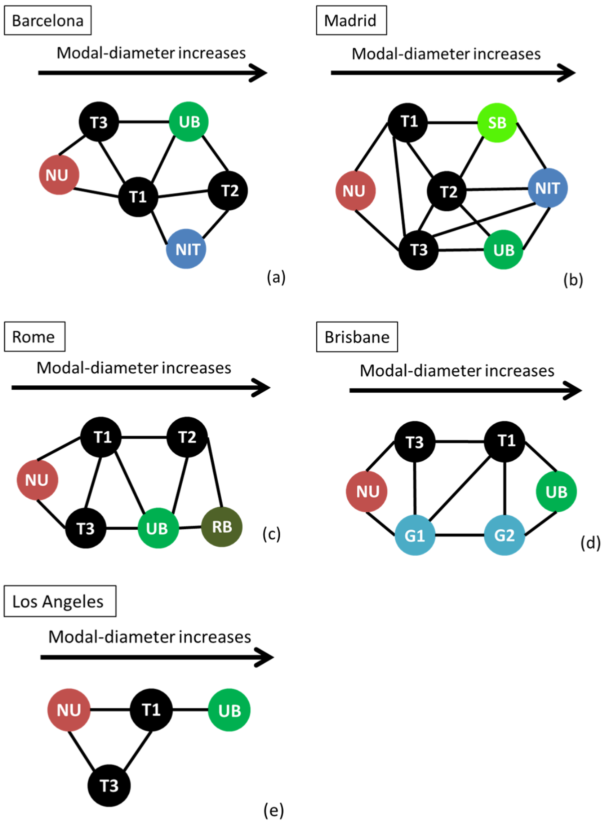

Figure 3. Cluster proximity diagram (CPD) for each selected city. In black are represented the Traffic clusters (T1, T2, T3), in green the background clusters (UB, SB, RB), in red the nucleation cluster (NU), in dark blue the Nitrate cluster (NIT) and in light blue the growth clusters (G1, G2) for: **(a)** Barcelona, **(b)** Madrid, **(c)** Rome, **(d)** Brisbane and **(e)** Los Angeles.

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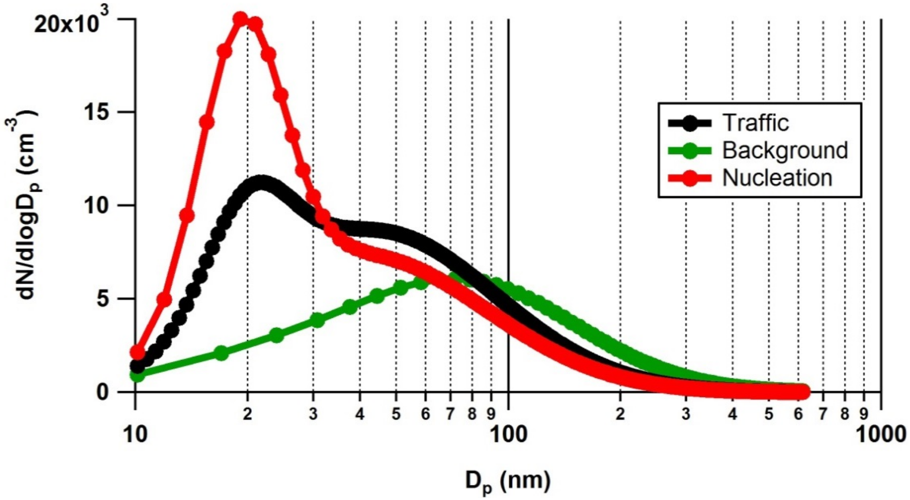

Figure 4. Average aerosol size distributions for each *k*-Means cluster category: Traffic, Background and Nucleation.

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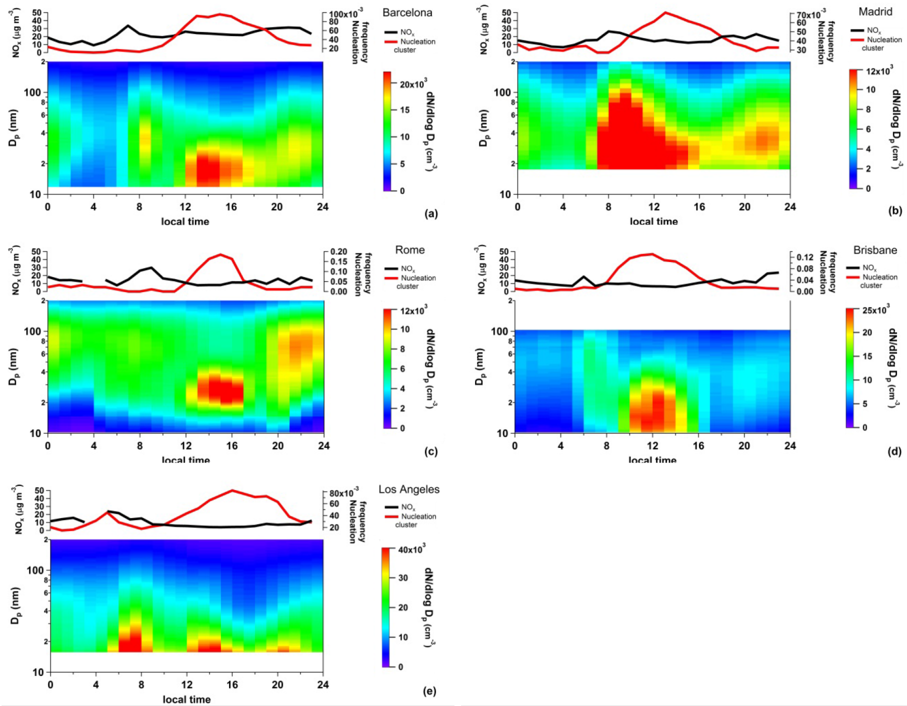

Figure 5. Daily average SMPS size distribution on a nucleation day at each selected city, NO_x average concentration and the frequency of occurrence of the Nucleation cluster for: **(a)** Barcelona, **(b)** Madrid, **(c)** Rome, **(d)** Brisbane and **(e)** Los Angeles. Please note that NO_x concentrations 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.

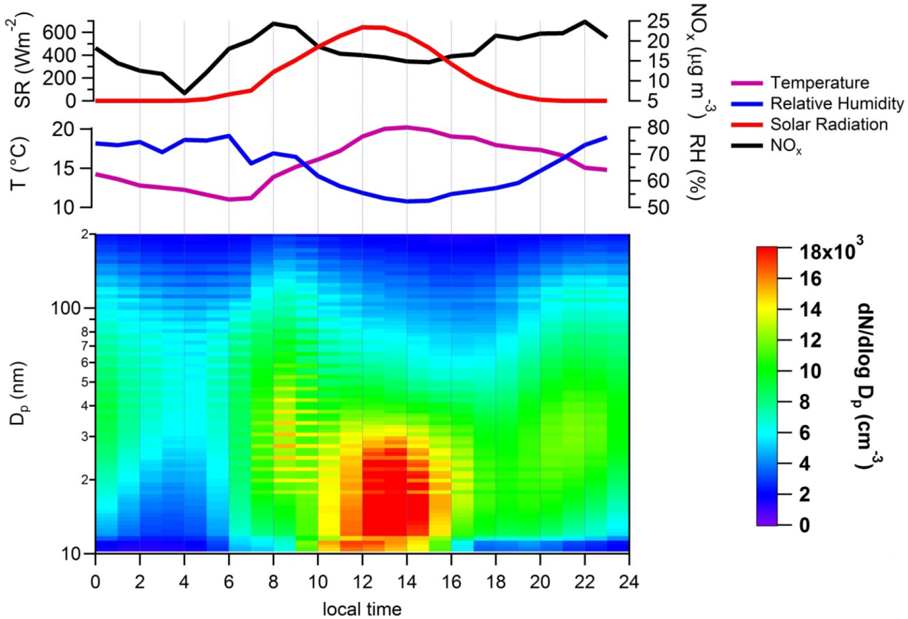

Figure 6. Daily average PN size distribution, temperature, relative humidity, solar radiation and NO_x levels on a nucleation day using data from Barcelona, Madrid, Rome and Brisbane.

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