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8 west Mediterranean basin
9 [Second round of reviewing:](#)

10

11 [We want to thank both Referee#2 and #3 for their suggestions, which have considerably](#)
12 [improved the manuscript. We have complemented the discussion as requested by Referee](#)
13 [#2 by including recent studies performed in high insolation urban environments around the](#)
14 [world, and softened specific sentences as required by Referee #3. Although traffic is the](#)
15 [main source of UFP in urban areas, in developed countries with high insolation urban](#)
16 [nucleation is often detected. However, in developing cities with also high insolation, the](#)
17 [higher concentration of pre-existing primary particles and thus an elevated condensation](#)
18 [sink do not favour nucleation. If primary particles were reduced, secondary processes](#)
19 [would likely increase in urban areas, therefore a further investigation of secondary particle](#)
20 [formation in urban areas is needed \(Wichmann et al., 2000\)](#)

21

22 Anonymous Referee #2

23 The revised paper has been modified significantly and the authors tried to address
24 reviewers remarks. However, to my opinion not all points were answered and modified in a
25 satisfying way, thus, more works needs to be done.

26

27 The re-arrangement of cities is okay to have more statistical significance.
28 In general, this paper is dealing with a topic: analysis of aerosol number size distributions
29 in cities which became very popular in the last years. Thus, the presentation and simple
30 analysis is not enough for a scientific publication, one also needs a good conclusion and
31 an answer to the question where can the results be used for? This is still a very weak part
32 of the present paper and some more effort should be put into drawing relevant
33 conclusions.

34

35 I would also like to see more comparison with other cities. There are many measurements
36 available over the past 20 years and at least some more from other countries should be

1 mentioned.

2 With some additional work on the points mentioned here the paper might be published in
3 ACP, but first its scientific relevance needs to be stated clearly.

4

5 Overall we have introduced almost 30 new references, and doubled the introduction and
6 the discussion in length. We believe this paper now has dramatically improved, and it is
7 put in the context of the most recent literature available.

8

9 Measurements:

10 What about the humidity in the inlet system? I read in the Brines et al, 2014 paper that no
11 dryer was used, was this the case also here? Was the sheath air dried? I think the
12 standard TSI-systems do not have a dryer included. Particularly under high humidities as
13 they may occur in the Mediterranean the hygroscopic growth could play a significant role
14 and should be discussed in the paper. This is a very crucial point for the data quality and
15 influences all conclusions.

16 R: Unfortunately no drier was used in the inlet systems of the different SMPS. We are
17 aware that a drier for each SMPS should have been used; however this was not possible
18 at the time of sampling. Nevertheless, all data were thoroughly checked to avoid possible
19 humidity influences. For example, in Rome the cabin was warmed during the cold months
20 to get RH<50%; during the warmer period, the data having minimum dew point
21 temperature larger than the cabin temperature (only the warmest morning hours of July
22 and August) were eliminated (Costabile et al., 2010). Using the k-Means clustering
23 analysis we have greatly simplified the aerosol size distributions in order to compare the
24 selected cities. The percentages of occurrence of the cluster at each site in addition to the
25 correlation with gaseous pollutants and meteorological parameters, we believe that the
26 resolved clusters are very robust.

27 The following text has been added:

28 “Although the use of aerosol drier is advisable (Swietlicki et al., 2008; Colbeck et al.,
29 2014), it was not possible at the time of sampling. Nevertheless, all data were thoroughly
30 checked to avoid possible humidity influences.”

31

1

2 Results:

3 Traffic cluster: I am not happy with the high number of clusters. For instance the traffic
4 clusters: T1 and T2 look very similar and T3 does not really fit to my opinion. It shows
5 strong indications for nucleation, e.g. has its maximum around noon and the small mean
6 diameter, thus I do not believe that it is related to traffic.

7 R: We believe the number of clusters is adequate, as they are associated with different
8 characteristics. For instance, the T1 cluster represents fresh vehicle emissions and T2
9 more aged. This is reflected in the different spectra shapes, size peaks and concentrations
10 of traffic emitted pollutants. Cluster number were already reduced following the procedure
11 described in the supporting information, thus the number of clusters presented in the paper
12 is regarded as suitable by the authors, as further merging of clusters would mean an
13 information loss. Regarding T3, although its occurrence at daytime and its size peaks
14 might indicate the presence of particles from photochemical nucleation events, the higher
15 concentration of traffic pollutants recorded for T3 in comparison to the NU cluster points
16 towards traffic emissions as its main source. Moreover, T3 shows an intermediate
17 occurrence time between morning traffic rush hour and the nucleation peak and also a
18 much lower PN in the nucleation mode and a higher concentration of particles in the large
19 Aitken-accumulation mode than the NU cluster.

20

21 The following text has been added to the manuscript:

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

29

30 As I already wrote in my first review: In the urban environment it might be hard to
31 distinguish between traffic-induced secondary aerosol formation and new particle
32 formation. In fact, both processes are induced by nucleation, even the precursors like
33 sulfuric acid might be the same. I strongly recommend to read this paper (Uhrner et al.,

1 Atmospheric Environment 41 (2007) 7440–7461) which shows nicely how nucleation and
2 growth happen after the tailpipe.

3 I do not like the answer of the authors in this point where they state that newly formed
4 particles in the exhaust of cars are generally treated as primary. This is not true and it has
5 to be discussed here. There are different mechanisms of new particle formation going on
6 in cities due to the variety of precursor gases and other conditions. But this needs to be
7 discussed and makes such a study in a city more difficult.

8 R: We agree with the reviewer that nucleation related to traffic emissions does occur after
9 the tailpipe, as exposed by Uhrner et al. (2007). Sulphuric acid and low-volatility organic
10 species are thought to be its gaseous precursors. Two main categories of nucleation
11 events have been reported in urban areas: traffic-related and photochemically driven.
12 These processes, although they might share some precursors such as SO₂ and low
13 volatility gases (which are related to traffic and industrial emissions among others) show
14 some differences. Nucleation after tailpipe is enhanced under low temperatures and
15 dilution processes that favour the nucleation of the high temperature emitted gaseous
16 precursors (Charron and Harrison, 2003; Uhrner et al., 2007). However, photochemical
17 nucleation is necessarily linked to intense solar radiation, as it will not take place even if
18 the gaseous precursor's concentrations are sufficient (Reche et al., 2011). In this case, the
19 highest occurrence of photochemical nucleation events is found at midday (highest
20 insolation), when low traffic emissions and low condensation sink are coupled with the
21 development of the boundary layer causing pollutants dilution.

22 In our study, all sampling sites were located in representative urban background
23 environments of each selected city, at a minimum 150 m distance from the nearest
24 trafficked roads. At this distance, Zhu et al. (2002) showed that PN had reduced drastically
25 in comparison to the roadside and its size distribution had evolved from a predominant
26 nucleation mode close to traffic to a bi-modal size distribution in the Aitken and
27 accumulation modes further downwind. Indeed, T1, which represents fresh traffic
28 emissions and includes both soot particles and traffic nucleated particles, shows a bimodal
29 distribution with peaks in the Aitken and accumulation modes (see Table 2 of the
30 manuscript).

31 However, the most distinctive feature that differentiates T1 from NU cluster is their daily
32 trend, reflecting morning and evening rush hour in the case of T1, and at midday peak for
33 NU inversely correlated with traffic flow and coinciding with the highest solar radiation.
34 Moreover, T1 shows the highest concentration of traffic related gaseous pollutants,

1 whereas NU shows the lowest. Thus, traffic-related nucleation particles and photochemical
2 nucleation particles clusters are perfectly distinct in our analysis.

3

4 I did not get the reason for the Summer background cluster? It is not mentioned in the
5 discussion later, thus: it is not important? Of course in all cities the background may play an
6 important role, but it is also very likely that the background is different. Maybe this is the
7 reason for the high number of clusters? If this is the case, maybe a common data analysis
8 for all cities is not reasonable and should be limited to similar cities only?

9 R: The background and specific case clusters have been unified under the same category
10 as to simplify the analysis and point out traffic and nucleation as the main sources of UFP
11 in urban environments with high insolation. Indeed background conditions may vary within
12 cities due both to local and regional sources, but were not further discussed in this paper.
13 Although it is a special case cluster, due to its unique characteristics its merging with the
14 Madrid urban background cluster was not found appropriate. This cluster might be subject
15 of analysis in future studies.

16 New particle formation has been observed in other European cities too with very similar
17 characteristics (e.g. in Leipzig, Germany). You should include such studies into your study.

18 R: An extended literature review was added to the manuscript and consequently
19 discussed. More than 30 papers have been added to the current version of the paper.

20 Another hint: Why don't you separate between weekends and weekdays? I expect a
21 completely different driving behavior and one can probably detect new particle formation
22 much clearer on weekends. Also the distribution of clusters is probably different due to the
23 different traffic behavior.

24 R: As suggested, a weekday/weekend analysis for each cluster at each city was
25 performed and added to the discussion:

26 "It is worth to note that weekday/weekend ratio was calculated for each cluster at each city
27 in order to analyse the impact of traffic/urban emissions on the clusters occurrence. The
28 highest average ratio (1.3) was found for the T1 cluster, strengthening its relation to fresh
29 traffic emissions. On the other hand, T2 and T3 clusters average ratio was 1-1.1, thus
30 pointing toward cleaner traffic conditions than T1, which occur both during weekdays and
31 weekends. The nucleation cluster was found to occur more often during weekends

1 (average ratio 0.9). The lowest ratio was recorded for the UB cluster during weekends
2 (average ratio 0.7) reflecting its clean nature. “

3
4 Page 20, line 12: How can you state that a NPF event is of regional type? This is not
5 possible to my opinion from one measurement site. The contour plots also do not show
6 any growth of particles which could be a hint for a regional event. I think it is very typical
7 for cities that NPF occurs but particles do not show a clear growth (banana-like). If you add
8 some more studies from other cities you can show this.

9 R: An example of the contour plots showing a growth of particles in the Brisbane site can
10 be seen in Cheung et al. (2011). Moreover, in Fig. 5c in the manuscript it can be observed
11 that in Brisbane nucleation events start in the morning, similarly to those reported as
12 regional nucleation type events by Dall'Osto et al. (2013). We have also added an
13 extended discussion on the urban and regional type events, as reported in Dall'Osto et al.
14 (2013) and cited and further discussed in Kumar et al. (2014) and Salma et al. (2015).

15 The following sentence has been added to the discussion:

16 “The city of Brisbane exhibits new particle formation events starting in the morning (see
17 Figure 5c), similar to the regional nucleation event types discussed in Dall'Osto et al.
18 (2013) as they are often followed by particles growth showing a banana-shape (Cheung et
19 al., 2011).”

20
21 One hypothesis for the small particles could be also that the particles were formed
22 somewhere else and transported by advection or vertical mixing due to convection. This
23 would explain why they appear at larger diameters and do not show up at the lower end of
24 SMPS. Also here, the investigation of new particle formation on weekends separately
25 could help!

26 R: Figures 5 and 6 show that the nucleation particles show up at the lower end of each
27 SMPS size range, with the exception on Rome, whose nucleation particles are indeed
28 transported from the Rome area and reach the site at a larger size. Therefore we believe
29 that particles are photochemically nucleated in the urban environment. The study of
30 Dall'Osto et al (2013) already discussed the different types of nucleation occurring within
31 the city and at regional level.

32 Overall, we would really like to thank reviewer #2. After this second round of reviewing, we
33 systematically tried our best to include most of the papers discussing clustering analysis of

1 urban aerosol size distributions and new particle formation in urban areas. Following this,
2 we have also changed the title and the context of the paper. By adding also the studies in
3 developing countries, we discuss what we see in developed high insolation urban
4 environments.

5

6

7

8 Anonymous Referee #3

9 The scientific level of new manuscript improved substantially due to the effort of the
10 authors in answering and discussing most of the arguments raised during the first round of
11 reviews. I consider the manuscript ready for publication in ACP only after the following
12 changes will be applied.

13

14 Among others, a major change from previous version is the replacement of the words
15 “Mediterranean climate urban environment” with the words “high insolation urban
16 environments”. As stated by the authors this “extended the climatic consideration” from a
17 particular climate (Mediterranean) to a more general one (high insolation). Moreover in the
18 revised manuscript conclusions are drawn from only 3 cities. These changes reinforce the
19 need to temper some strong statement. In particular, the sentence at page 4, lines 19-20,
20 the “study that will lead to obtaining general conclusions on nucleation events in high
21 insolation urban environments” should be revised and soften. Also the conclusive
22 sentence at page 19, lines 19-21 should include the caveat that this is valid for the 3 cites
23 of Barcelona, Madrid and Brisbane and not necessarily for urban areas under high solar
24 radiation.

25 R: page 4, lines 19-20 and page 19, lines 19-21 have been eliminated from the
26 manuscript.

27

28 References:

29 Charron, A. and Harrison, R. M.: Primary particle formation from vehicle emissions during
30 exhaust dilution in the roadside atmosphere, *Atmos. Environ.*, 37, 4109–4119, 2003.

31

32 Cheung, H.C., Morawska, L. and Ristovski, Z.D.: Observation of new particle formation in
33 subtropical urban environment, *Atmos. Chem. Phys.*, 11, 3823-3833, 2011.

1
2 Colbeck, I., Lazaridis, M.: *Aerosol Science: technology and Application*. First Edition ©
3 2014 John Wiley & Sons, Ltd. ISBN: 978-1-119-97792-6.
4
5 Dall'Osto, M., Thorpe, A., Beddows, D. C. S., Harrison, R. M., Barlow, J. F., Dunbar, T.,
6 Williams, P. I., and Coe, H.: Remarkable dynamics of nanoparticles in the urban
7 atmosphere, *Atmos. Chem. Phys.*, 11, 6623–6637, 2011b.
8
9 Dall'Osto, M., Querol, X., Alastuey, A., O'Dowd, C., Harrison, R.M., Wenger, J. and
10 Gómez Moreno, F.J.: On the spatial distribution and evolution of ultrafine particles in
11 Barcelona, *Atmos. Chem. Phys.*, 13, 741-759, doi:10.5194/acp-13-741-2013, 2013.
12
13 Kumar, P., Morawska, L., Birmili, W., Paasonen, P., Hu, M., Kulmala, M., Harrison, R.M.,
14 Norford, L. and Britter, R.: Ultrafine particles in cities, *Environ. Int.*, 66, 1-10, 2014.
15
16 Liu, Z.R., Hu, B., Liu, Q., Sun, Y., Wang, Y.S.: Source apportionment of urban fine particle
17 number concentration during summertime in Beijing, *Atmos. Environ.*, 95, 359-369, 2014.
18
19 Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodríguez, S.,
20 González, Y., Fernández-Camacho, R., de la Rosa, J., Dall'Osto, M., Prévôt, A. S. H.,
21 Hueglin, C., Harrison, R. M., and Quincey, P.: New considerations for PM, Black Carbon
22 and particle number concentration for air quality monitoring across different European
23 cities, *Atmos. Chem. Phys.*, 11, 6207–6227, 2011.
24 Salma, I., Fűri, P., Németh, Z., Balásházy, I, Hofmann, W. and Farkas, A.: Lung burden
25 and deposition distribution of inhaled atmospheric urban ultrafine particles as the first step
26 in their health risk assessment, *Atmos. Environ.* 104, 39-49, 2015.
27
28 Swietlicki, E., Hansson, H.-C., Hämeri, K., Svenningsson, B., Massling, A., McFinnigans,
29 G., McMurray, P.H., Petäjä, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E.,
30 Baltensperger, U., Rissler, J., Wiedensohler, A. and Kulmala, M.: Hygroscopic properties
31 of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in
32 various environments-a review, *Tellus*, 60B, 432-469, 2008.
33
34 Uhrner, U., von Lowis, S., Vehkamäki, H., Wehner, B., Brasel, S., Hermann, M.,
35 Stratmann, F., Kulmala, M. and Wiedensohler, A.. Dilution and aerosol dynamics within a
36 diesel car exhaust plume – CFD simulations of on-road conditions, *Atmos. Environ.*, 41,
37 7440–7461, 2007.
38
39 Wang, Z. B., Hu, M., Sun, J. Y., Wu, Z. J., Yue, D. L., Shen, X. J., Zhang, Y. M., Pei, X. Y.,
40 Cheng, Y. F., and Wiedensohler, A.: Characteristics of regional new particle formation in
41 urban and regional background environments in the North China Plain, *Atmos. Chem.*
42 *Phys.*, 13, 12495-12506, doi:10.5194/acp-13-12495-2013, 2013a.
43

1 Wichmann, H.E., Spix, C., Tuch, T., Wölke, G., Peters, A., Heinrich, J., Kreyling, W. and
2 Heyder, J.: Daily mortality and fine and ultrafine particles in Erfurt, Germany. Part I: Role of
3 particle number and particle mass, HEI Research Report, 98, 2000.

4
5 Zhu, Y., Hinds, W.C., Kim, S. and Sioutas, C.: Concentration and size distribution of
6 ultrafine particles near a major highway, Journal of the air & waste management
7 association, 52(9), 1032-1042, 2002.

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1

2 **Traffic and nucleation events as main**

3 **sources of ultrafine particles in high**

4 **insolation developed world cities**

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Eliminado: Frequency of new particle formation events in high insolation urban environments

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8 G.P.⁷, Salimi, F.⁸, Morawska, L.⁸, Sioutas, C.⁹, Querol, X.¹

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29

30 **Abstract**

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1 |
2 | Road traffic emissions are often considered the main source of ultrafine particles (UFP,
3 | diameter smaller than 100 nm) in urban environments. However, recent studies worldwide
4 | have shown that, - in high insolation urban regions at least, - new particle formation events
5 | can also contribute to UFP. In order to quantify such events we systematically studied
6 | three cities located in predominantly sunny environments: Barcelona (Spain), Madrid
7 | (Spain) and Brisbane (Australia). Three long term datasets (1-2 years) of fine and ultrafine
8 | particle number size distributions (measured by SMPS, Scanning Mobility Particle Sizer)
9 | were analysed. Compared to total particle number concentrations, aerosol size
10 | distributions offer far more information on the type, origin and atmospheric evolution of the
11 | particles. By applying *k*-Means clustering analysis, we categorized the collected aerosol
12 | size distributions in three main categories: "Traffic" (prevailing 44-63% of the time),
13 | "Nucleation" (14-19%) and "Background pollution and Specific cases" (7-22%),
14 | Measurements from Rome (Italy) and Los Angeles (California) were also included to
15 | complement the study. The daily variation of the average UFP concentrations for a typical
16 | nucleation day at each site revealed a similar pattern for all cities, with three distinct
17 | particle bursts. A morning and an evening spike reflected traffic rush hours, whereas a
18 | third one at midday showed nucleation events. The photochemically nucleated particles
19 | burst lasted 1-4 hours, reaching sizes of 30-40 nm. On average, the occurrence of particle
20 | size spectra dominated by nucleation events was 16% of the time, showing the importance
21 | of this process as a source of UFP in urban environments exposed to high solar radiation.
22 | On average, nucleation events lasting for 2 hours or more occurred on 55% of the days,
23 | this extending to >4hrs in 28% of the days, demonstrating that atmospheric conditions in
24 | urban environments are not favourable to the growth of photochemically nucleated
25 | particles. In summary, although traffic remains the main source of UFP in urban areas, in
26 | developed countries with high insolation urban nucleation events are also a main source of

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(13-22%),
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specific

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of the studied cities, particle number
concentration averaged daily profiles
for the whole study periods clearly
showed the same three particle bursts.
This reveals nucleation events as a
relevant contributor to the average daily
urban exposure to UFP in high
insolation urban environments.
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1 UFP. If traffic-related particle concentrations are reduced in the future, nucleation events
2 will likely increase in urban areas, due to the reduced urban condensation sinks.

4 **1 Introduction**

5
6 Largely populated urban areas are hotspots of urban air pollution due to the many and
7 highly complex pollution sources of particulate matter and gaseous co-pollutants. Current
8 regulations address the amount of ambient particulate matter expressed as a mass
9 concentration of particles, and not particle number concentrations. However, the European
10 Union (EU) has recently taken initial steps to set particle number concentrations emission
11 regulations for vehicular emissions (EU, 2012). It is worthy of note that ultrafine particles -
12 the main source of particles by number - are ubiquitous in urban environments (Kumar et
13 al., 2014), and typically are of high number concentration and negligible mass. They have
14 a great potential for lung deposition and are associated with respiratory and cardiovascular
15 diseases (Atkinson et al., 2010; Oberdorster et al., 2005). There is increasing scientific
16 evidence that removal of particles deposited in the lung is size-related (Salma et al., 2015).
17 A number of studies have focused on the source apportionment of number and size
18 characteristics of submicron particles in urban ambient air (Pey et al., 2009; Costabile et
19 al., 2009; Harrison et al., 2011; Dall'Osto et al., 2012; Hussein et al., 2014; Liu et al., 2014;
20 Salimi et al., 2014).

21 The main source of primary ultrafine particles in urban area is traffic activity. These
22 particles can be formed in the engine or in the atmosphere after emission from the tailpipe
23 (Shi and Harrison, 1999; Charron and Harrison, 2003). Primary particles related to traffic
24 are emitted during the dilution and cooling of road vehicle exhaust (Charron and Harrison,
25 2003; Kittelson et al., 2006) or as carbonaceous soot agglomerates formed by fuel

Eliminado: Ultrafine particles are ubiquitous in urban environments (Kumar et al., 2014). Due to their high number concentration and negligible mass, they have a great potential for lung deposition and are associated with respiratory and cardiovascular diseases (Atkinson et al., 2010; Oberdorster et al., 2005). Ultrafine particles can have a primary or a secondary origin

1 combustion (Kittelson, 1998; Shi et al., 2000). Other combustion sources such as waste
2 incinerators are minor contributors to UFP loading in urban environments (Buonanno and
3 Morawska 2015). Nucleation mode particles related to traffic are formed behind the
4 exhaust tailpipe as the exhaust gases are diluted and cooled with ambient air (Charron
5 and Harrison, 2003). The most crucial aspect of particle formation behind the exhaust
6 tailpipe is the three-dimensional representation of the dilution pattern, which involves
7 varying length and time scales (Zhu et al., 2002; Uhrner et al., 2007; Wehner et al., 2009;
8 Huang et al., 2014). Strictly speaking, these particles are secondary, but as they form so
9 close to source, most works regard them as primary.

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11 Additionally, new particle formation of regional origin (Kulmala et al., 2004; Wehner et al.,
12 2007; Costabile et al., 2009) has also been detected in urban areas. This in contrast to
13 what was assumed in the past, which is that photonucleation events only occur in
14 background and regional environments such as clean coastal (O'Dowd et al., 2010), forest
15 areas (Boy and Kulmala, 2002), semi-clean savannah (Vakkari et al., 2011), high altitude
16 locations (Sellegri et al., 2010) and regional background sites (Wiedensohler et al., 2002).

Eliminado: Secondary particles are formed through nucleation processes of gaseous precursors such as SO₂ and NH₃ in neutral or ion induced processes

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It has been often assumed that

17 This is usually attributed to the fact that such natural environments are characterised by a
18 low condensation sink (CS), thus facilitating nucleation. By contrast, urban environments
19 are often characterised by high CS, so that a lower frequency of nucleation events is
20 expected. Nevertheless, there are studies showing that these events in fact can be
21 detected in urban areas, as originally demonstrated in Atlanta, USA (Woo et al., 2001),
22 Birmingham, UK (Alam et al., 2003) and Pittsburgh, USA (Stanier et al., 2004), and
23 subsequently in many cities worldwide (Pey et al., 2008, 2009; Wu et al., 2008; Costabile
24 et al., 2009; Rimnácová et al., 2011; Salma et al., 2011; Dall'Osto et al., 2013; Betha et al.,
25 2013; Cheung et al., 2013; Brines et al., 2014).

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1 High insolation and wind speed, low relative humidity, available SO₂ and low pre-existing
2 particle surface area are common features that enhance new particle formation events
3 (Kulmala and Kerminen, 2008), characterised by a great increase in particle number
4 concentrations (PN) in the nucleation mode and subsequent particle growth, if conditions
5 are favourable. Within Northern Europe, nucleation events in many urban areas ~~are not~~
6 very often detected (Alam et al., 2003; Wegner et al., 2012; von Bismarck-Osten et al.,
7 2013). However, Reche et al. (2011) showed that a different behaviour was observed in
8 southern European cities, where new particle formation processes at midday did occur
9 with higher frequency than in northern European cities. The main cause for this difference
10 is likely to be the higher intensity of solar radiation in the Southern European areas, and/or
11 possible site specific chemical precursors.

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

25 Hence, the objective of this study is to categorise sources of UFP in urban environments
26 situated in temperate regions affected by high solar radiation levels. Specifically, we aim to

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The

1 assess the frequency and influence of nucleation events on UFP levels and variability, as
2 well as the atmospheric conditions facilitating such events. Reche et al. (2011)
3 demonstrated that with aerosol number concentration (PN) and BC concentration
4 measurements, useful information can be drawn on the differences in primary emissions
5 and nucleation enhancements across European cities. The present work considers not
6 only PN, but also aerosol size distribution. This is one of the most important properties of
7 particles, which helps in understanding aerosol dynamics, as well as determining their
8 sources (Harrison et al., 2011; Salimi et al., 2014; Beddows et al., 2015). In the present
9 work, size-resolved particle number concentration measurements using a Scanning
10 Mobility Particle Sizer, (SMPS, see Table S2 for details) sampled in a number of urban
11 areas are presented and discussed. The complexity of the data is further reduced by
12 applying *k*-Means clustering analysis (Beddows et al., 2009; Dall'Osto et al., 2011b and
13 2012; Sabaliauskas et al., 2013; Brines et al., 2014; Salimi et al., 2014). This clustering
14 technique classifies aerosol size spectra into a reduced number of categories or clusters
15 that can be characterised considering their size peaks, temporal trends and meteorological
16 and gaseous pollutants average values (Beddows et al., 2009). Salimi et al. (2014)
17 showed that the *k*-Means clustering technique was found to be the preferred one among
18 several used, and Väänänen et al. (2013) showed that clustering analysis is a good tool for
19 studying aerosol dynamics and new particle formation events. In other words, we use a
20 wide aerosol size distribution (10.2-17.5/101.8-615.3nm) and not only the total particle
21 number concentrations to assess the source of ultrafine particles in the urban atmosphere,
22 leading to a better apportionment. The identification of the main pollution sources
23 contributing to ultrafine particles affecting urban environments enables quantitative
24 estimation of the temporal prevalence of each source.

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Eliminado: Although a number of studies have addressed this issue, we aim at an inclusive study that will lead to obtaining general conclusions on nucleation events in high insolation urban environments.

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

8 **2 Methodology**

9 **2.1 Site locations**

10 Following previous work (Reche et al., 2011; Kumar et al., 2014) we selected four cities
11 (Barcelona, Madrid, Rome and Los Angeles), all located in Mediterranean climatic regions,
12 according to the Köppen climate classification (Figure 1). The Mediterranean climate is
13 categorised as *dry-summer subtropical* (type Csa/b) due to its mild winters and warm
14 summers with scarce rainfall. It is characterised by annual average temperatures of 12-
15 18°C, with dominant clear sky conditions (annual global irradiance intensity of 180-190
16 Wm⁻²). Precipitation is concentrated in autumn and spring and is very scarce during
17 summer; its annual average is about 600 mm. Although it prevails in the coastal
18 Mediterranean Sea Basin areas, it is also present in other parts of the world, such as
19 south-western USA, the west and southern Australia coast, south-western South Africa
20 and central Chile (see Figure 1). Three cities in the western Mediterranean Basin were
21 selected for this study: Barcelona, Madrid and Rome. For the American continent the city
22 of Los Angeles was chosen (it is also located in a Mediterranean climate region). Finally,
23 the city of Brisbane (Australia) was also included. Its climate is categorised as *humid*
24 *subtropical* (type Cfa) due to the higher mean annual rainfall (1150 mm versus 600 mm for
25 the Mediterranean climate), although otherwise presents many climatological similarities to

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

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1 the Mediterranean regions with mild winters and warm summers with prevalent sunny days
2 (average annual global irradiance of 208 Wm⁻²). A detailed description of the five selected
3 cities is given below:

4 1) Barcelona (BCN), Spain: located on the north-western Mediterranean basin it has 1.7
5 million inhabitants although the metropolitan area exceeds 4 million. The SMPS sampling
6 site (Palau Reial) can be classified as urban background and is located close (350 m) to a
7 major highway (Diagonal Avenue: 90 000 vehicles per working day), which is primarily
8 used by commuters (see Table S1). Previous work in the study area has demonstrated
9 that 65-69% of ultrafine particles are emitted by traffic and that photonucleation events
10 contribute remarkably to the annual average total PN (Pey et al., 2008, 2009; Dall'Osto et
11 al., 2012).

Eliminado: Road traffic is the major emission source, although industrial, domestic, shipping emissions and occasional Saharan dust outbreaks also contribute to increase ambient PM levels.

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

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20 3) Brisbane (BNE), Australia: located on the eastern Australian coast, it has two million
21 inhabitants although the metropolitan area accounts for 3 million. Traffic exhaust
22 emissions are the main pollution source, although plumes coming from the airport, harbour
23 and industrial facilities can also contribute. The SMPS was deployed on the top of a
24 building owned by the Queensland University of Technology (QUT), in an area considered
25 as urban background (see Table S1). Previous work in the study area (Cheung et al.,
26 2011) analysed one year of SMPS data in the ultrafine range, focusing on the nucleation

1 processes in the urban background. They reported three main diurnal PN peaks; two
2 related to traffic rush hours and a third one occurring at midday related to nucleation.

3 4) Rome (ROM), Italy: located 24 km inland from the Mediterranean Sea, it features 2.7
4 million inhabitants although the metropolitan area accounts for 4 million. The sampling site
5 is located in Montelibretti, 30 km NE from the Rome city centre (Table S1). Although
6 considered as a regional background site, it is regularly impacted by pollutants transported
7 from the area of Rome, due to the sea-breeze circulation (Ciccioli et al., 1999). Previous
8 work in the study area (Costabile et al., 2010) applied a clustering analysis (Principal
9 Component Analysis, PCA) on two years of SMPS data, reporting three main factors: an
10 aged nucleation mode, an Aitken mode and an accumulation mode factor (21%, 40% and
11 28% of the variance, respectively).

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

22 Although the selected cities are located in similar climatic environments, some differences
23 regarding meteorological conditions were encountered (see Table1). All cities show mild
24 annual temperatures, ranging from 15°C in Madrid (due to its inland location) to 20°C in
25 Brisbane (due to its latitude, closer to the equator, see Figure 1). Relative humidity varies
26 by 10% across the cities, showing highest values in Brisbane (72%). This is probably

1 related to the higher precipitation rate registered in this city (1072 mm), two times higher
2 than in BCN, MAD or LA (430-450mm). As expected, the highest average annual values of
3 solar radiation are recorded in Brisbane and the lowest in Madrid ($240\pm 337 \text{ Wm}^{-2}$ and
4 $182\pm 265 \text{ Wm}^{-2}$, respectively). UFP concentrations (common size range 17.5-100 nm)
5 showed lowest levels in Rome (due to the location of the sampling site, $5000\pm 3000 \text{ cm}^{-3}$),
6 followed by Brisbane, Madrid and Barcelona ($6000\pm 7000 \text{ cm}^{-3}$, $7000\pm 8000 \text{ cm}^{-3}$ and
7 $7500\pm 5000 \text{ cm}^{-3}$, respectively). The highest concentrations corresponded to the city of LA
8 ($12000\pm 7000 \text{ cm}^{-3}$), probably due to the proximity to the freeway and the limited sampling
9 time (3 months).

10 In addition to meteorological features, emission sources also have an impact on UFP in
11 urban environments, especially traffic related pollutants. The vehicle fleet composition is
12 not homogeneous among the sampling sites, as a tendency towards dieselization has
13 been experienced in some European countries over the last years, especially in Spain
14 (Amato et al., 2009), where 55% of vehicles are diesel-powered versus 44% gasoline
15 (Dirección General de Tráfico, 2015). In Italy 37% of the vehicles used diesel fuel and 62%
16 used gasoline in 2007 (Istituto Nazionali di Statistica, 2009). On the other hand, in the USA
17 or Australia the diesel share represents only around 20% (Gentner et al., 2012; Australian
18 Bureau of Statistics, 2014). Diesel vehicle engines are known to emit much higher PN than
19 gasoline ones (Harris and Maricq, 2001), which might imply a higher concentration of
20 primary UFP in European countries in comparison to the USA and Australia. Another
21 relevant difference between the cities relates to their urban structure. While both Brisbane
22 and Los Angeles are extensively suburbanised cities with relatively low population
23 densities, favouring dilution and diffusion of pollutants, southern European cities are dense
24 urban agglomerates that favour the trapping and accumulation of pollutants. The lower
25 concentrations of UFP in Brisbane in comparison with European cities are therefore likely
26 due to lower primary diesel emissions and higher precipitation rates, coupled with higher

1 diffusion and dilution of pollutants due to the urban geography of the city. In the case of
2 Madrid and Barcelona, the higher proportion of diesel vehicles together with the high urban
3 density leads to an increase of UFP concentrations. In the case of Los Angeles, the high
4 readings are probably due to both the proximity to the traffic source and the reduced
5 sampling period (3 months). Given these differences between the cities, we nevertheless
6 view the climatic similarities to be strong enough to consider the urban background
7 environments in which the data have been sampled to be broadly comparable.

8 In order to show averaged annual results we only considered in this study the cities of
9 Barcelona, Madrid and Brisbane for several reasons. In Rome, the sampling site is not
10 located in an urban environment, although it is affected by the Rome pollution plume. The

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11 monitoring sites in the cities of Barcelona, Madrid, Brisbane and Los Angeles were
12 classified as urban background, whereas the one in Rome was further away from the city.

13 Regarding Los Angeles only three months of measurements were available, which was not
14 sufficient for studying the annual trends. However, we believe the sites of Rome and Los
15 Angeles add some important supporting information to further validate our findings.

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Eliminado: In spite of these limitations, we are able to demonstrate from the data that the atmospheric processes affecting the other 3 cities do also occur in ROM and LA.

16

17 2.2 Measurements

18 2.2.1 Particle number size distributions

19 The detailed characteristics of the sampling sites, sampling periods, SMPS models and
20 size ranges at each city can be seen in Tables S1 and S2. Although the use of aerosol
21 drier is advisable (Swietlicki et al., 2008; Colbeck et al., 2014), it was not possible at the
22 time of sampling. Nevertheless, data were thoroughly checked to avoid possible humidity
23 influences (Costabile et al., 2010). The SMPS low-cut point ranged from 10.2 nm to 17.5
24 nm whereas the SMPS high-cut point varied from 101.8 to 615.3 nm. The lack of
25 measurements below 10 nm does not allow for proper identification of the start of new

Eliminado: 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.

1 particle formation events, therefore our so-called “nucleation events” reflect
2 photochemically nucleated particles that have grown over the low-cut detection limits of
3 each instrument. In addition, such events were evaluated visually by inspecting the trends
4 of the SMPS size distributions. More information reporting a detailed analysis of the
5 aerosol size distributions used in this work can be found in previous studies (Madrid:
6 Gómez-Moreno et al., 2011; Brisbane: Cheung et al., 2011; Rome: Costabile et al., 2010;
7 Los Angeles: Hudda et al., 2010). Due to the different time resolution of each instrument,
8 all measurements were averaged to 1 hour resolution. All data herein reported should be
9 read as local time.

10

11 **2.2.2 Meteorological parameters and other air pollutants**

12 Meteorological (temperature, relative humidity, wind components and solar radiation),
13 gaseous pollutants (NO, NO₂, O₃, CO, SO₂) and other parameters (PM_x, PN, black carbon
14 and particulate nitrate concentrations) were obtained at the site or from the closest
15 available air quality station (see Table S3). These data were averaged to 1 hour resolution
16 to match the SMPS measurements.

17

18 **2.3 Data analysis (*k*-Means)**

19 The large amount of data presented in this work (31,448 hours distributed across five
20 sites) was simplified by applying *k*-Means clustering analysis (Beddows et al., 2009). This
21 methodology has already been successfully applied to a number of studies involving one
22 (Dall’Osto et al., 2012) or multiple monitoring sites (Dall’Osto et al., 2011**b**; Brines et al.,
23 2014). In a nutshell, this method creates manageable groups of clusters that can be
24 classified into aerosol size distributions types (i.e. characteristic of emission or formation
25 processes) and permits a simplification of the data analysis that facilitates its

1 interpretation. To account for the uncertainty of the method, the confidence limits μ (99.9%
2 confidence level) were calculated for all the cluster size distributions at each city, and
3 uncertainty bands were plotted around each cluster size distribution. A detailed description
4 of the method can be found in the supplementary information.

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5 **3 Results**

6 **3.1 *k*-Means clustering**

7 A *k*-Means clustering analysis was performed on each of the five SMPS data sets,
8 resulting in a number of representative clusters for each city that ranged between 7 and
9 15. After careful consideration, such results were further simplified to 4-7 clusters per
10 monitoring site (see Figure 2b-d, 3b-c). For further information regarding cluster number
11 reduction refer to the supplementary material. As recently discussed in Hussein et al.
12 (2014), it is not prudent to describe the size distributions with either too few or too many
13 clusters. Few clusters (2-4) are not enough to explain variations and detailed differences in
14 the particle number size distributions observed in the urban atmosphere. However, using
15 too many (>10) clusters often makes the aerosol source attribution more challenging. It is
16 important to note that the different aerosol size distribution clusters were merged not only
17 upon their similar size distributions among each other but also by considering strong
18 correlations with other physical and chemical parameters obtained with other instruments
19 (Beddows et al., 2009; Dall'Osto et al., 2011a). Additionally, the reduction to three more-
20 generic classifications, while not based on statistics, is based on existing knowledge of
21 distributions typically observed and associated with these categories. The average aerosol
22 size distributions of the three aerosol categories (obtained by averaging the SMPS clusters
23 of each individual category) are presented in Fig. 3. The uncertainty bands plotted for each
24 cluster (Figs. 2b-d and 3b-c) show the 99.9% confidence limits for the hourly size
25

1 distributions contained within each cluster. This means that with a probability of 99.9%, all
2 hourly spectra contained in each cluster are found within the uncertainty bands. The fact
3 that none of the uncertainty bands of the spectra overlap over the full size range at any of
4 the sites reflects the robust cluster classification achieved by *k*-Means analysis. To further
5 characterise each *k*-Means cluster, its corresponding size peaks were extracted; and
6 hourly, weekly and annual cluster trends were analysed. Moreover, the corresponding
7 average values of meteorological parameters and available air pollutants for each cluster
8 at each site were calculated. The analysis of each cluster characteristics allows its
9 classification into different categories depending on the main pollution source or process
10 contributing to it.

11 The majority of the clusters were found common to most of the cities, although showing
12 some site specific characteristics depending on the location of the site (proximity to
13 pollution sources), the sampling size range (low-cut 10.2-17.5 nm and upper-cut 101.8-
14 615.3 nm, see Table S2) and the particular emission and atmospheric features of each city
15 (see Figs. 2b-d and 3b-c). To further simplify the results, the clusters have been carefully

16 divided in three main categories: "Traffic", "Nucleation" and "Background pollution and
17 Specific cases". The most relevant categories common to all sites are Traffic and
18 Nucleation, which display very different characteristics. Broadly, Traffic clusters dominate
19 the aerosol size distributions during rush hours, showing very high NO_x levels. In contrast,
20 Nucleation clusters are seen at midday, under high temperature, solar radiation and ozone
21 levels and low NO_x levels. Detailed features of each *k*-Means size distributions can be
22 found in Table 2, S4, S5, S6 and Figures 2 and 3. Finally, it is important to remember that
23 the clustering results can provide a much higher amount of information than that presented
24 here. Nevertheless, the objective of this study is to present main aerosol size distribution
25 categories in order to quantify the impact of photochemical nucleation processes in urban
26 environments under high solar radiation. Therefore, the following results are focused on

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Eliminado: due to the limitations they present (site location and limited data availability, respectively) will be

1 the cities of Barcelona, Madrid and Brisbane. Results from Rome and Los Angeles are
2 herein used only to complement the discussion, given their limitations (site location and
3 limited data availability, respectively).

5 3.1.1 Traffic-related clusters

6 - Traffic 1 (T1): this cluster can be seen at all monitoring sites, occurring 27-24% of the
7 time (Table S4). It exhibits a bimodal size distribution, as typically found in vehicle
8 exhausts, with a dominant peak at 20-40 nm (traffic-related nucleated particles) and
9 another at 70-130 nm (soot particles) (see Table 2). Its diurnal trends are driven by traffic
10 rush hours and display very high levels of traffic pollutants, such as NO, NO₂, BC and CO
11 (see Fig. S1a and S2). Regarding particle mass concentrations, T1 is associated with high
12 values of PM₁₀ (see Fig. S2). We attribute this cluster to freshly emitted traffic particles.

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

20 This change can be appreciated for each city in Figure 2. The evolution of these aerosol
21 size distribution modes attributed to traffic have already been widely discussed in previous
22 studies (Dall'Osto et al., 2011; Dall'Osto et al., 2012; Brines et al., 2014).

23 - Traffic 3 (T3): this traffic related cluster was found in all the monitored cities 11-20% of
24 the time (see Table S4). It presents a bimodal size distribution, with a low peak in the
25 nucleation mode at 10-20 nm and a main peak at 50-90 nm (see Table 2). It occurs

1 throughout all day, with a peak during daytime, and it is associated with the lowest
2 pollution levels of all the Traffic clusters (see Fig. S1a). The shift to smaller sizes of the 20-
3 40 nm peak of T1 and T2 towards the nucleation mode in T3 might indicate particle
4 evaporation in Barcelona, Madrid and Brisbane (see Fig. 2b, c, d). More information on the
5 evolution of traffic related cluster T1-T2 towards traffic related cluster T3 can be found in
6 Brines et al. (2014), where aerosol size distribution modes simultaneously detected at four
7 monitoring sites during SAPUSS were reported. As recently discussed in Kumar et al.
8 (2014), the volatile nature of the traffic nucleation mode particles raises issues in relation
9 to their reliable measurement and may also enhance their spatio-temporal variability
10 following their emission into the atmospheric environment (Dall'Osto et al., 2011b). A
11 traffic- related cluster peaking during noontime was also related to the extension of the
12 morning traffic peak, which is similar to the diurnal variation of NO_x (Liu et al., 2014). The
13 pattern of this factor is similar to the local traffic factor found in Beijing in previous study
14 (Wang et al., 2013a).

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16 **3.1.2 Nucleation cluster**

17 - Nucleation (NU): the Nucleation cluster was found to be common to all sites - stressing
18 the importance of the occurrence of new particle formation processes in high insolation
19 urban environments (see Table S4). It occurs between 14 and 19% of the measured
20 periods and has a dominant nucleation mode peak in the range 10-20 nm and a minor size
21 peak in the Aitken mode at 50-80 nm (see Table 2), the latter being attributed to
22 background aerosols. NU is observed at midday or early afternoon more intensely during
23 spring and summer (see Fig. S1b). This cluster is generally characterised by very high
24 solar irradiance, high wind speed and low concentration of traffic pollutants (see Fig. S2).
25 The PN/NO_x ratio from 8 a.m. to 12 a.m. was calculated for the Nucleation and Traffic 1
26 clusters for each city. In all cases it was found to be higher for the Nucleation than for the

1 Traffic 1 clusters, highlighting both the clean atmospheric conditions favouring nucleation
2 (low NO_x levels) and the contribution of nucleated particles to PN.

3.1.3 Background pollution and Specific cases clusters

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6 - Urban Background (UB): the Urban Background cluster can be observed at all three sites
7 6-22% of the time (see Table S4). The size distributions present a bimodal peak at 20-40
8 nm and at 60-120 nm (see Table 2). At Barcelona and Madrid - cities highly influenced by
9 road traffic emissions - the dominant peak is the finest one, whereas in Brisbane the larger
10 peak prevails (see Table 2). Urban background clusters were usually observed during the
11 night time, associated with relatively clean atmospheric conditions in the urban
12 environment (see Fig. S1a and S2).

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

17 - Nitrate (NIT): this cluster was observed in the two Spanish cities, occurring 7% of the
18 time in Barcelona and 10% of the time in Madrid. This cluster is characterised by its
19 prevalence at night during the colder months (see Fig. S1b). Moreover, in Madrid a minor
20 peak was also seen during midday. Although the Nitrate cluster occurs more frequently at
21 night, photochemically induced nitrate formation accounts for higher mass concentrations
22 during the day, especially in winter in Madrid (Gómez-Moreno et al., 2007; Revuelta et al.,
23 2012).

24 The two size distributions associated with nitrate in Barcelona and Madrid are unimodal
25 although presenting different modes. BCN_NIT shows a finer mode at 36±1 nm, whereas

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3.1.3 Nucleation cluster¶

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

3.1.4 Specific case clusters¶

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

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

Another way of looking at the *k*-Means results is through the Cluster Proximity Diagram (CPD), which is obtained using the Silhouette Width (Beddows et al., 2009). This diagram positions each cluster according to the similarity with the rest of the clusters (Figure 2e-g). The closer nodes represent similar clusters, although they are not sufficiently alike to form a new cluster. Conversely, the more distant nodes represent the most dissimilar clusters and are located further apart. The average cluster modal diameter increases from left to right.¶

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

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1 environment, aerosol size distributions were only measured from September to December
2 (see Table S2). Two Traffic clusters and an Urban Background cluster were identified
3 (representing 61% and 6% of the time, respectively), reflecting the proximity of the
4 sampling site to main roads. The Nucleation cluster was found to occur 33% of the time,
5 due to the enhancement of photochemical nucleation events during warm months (see
6 Table S4).

7 **3.3 k-Means clustering results explained by the cluster proximity diagram**

8 Another way of looking at the k-Means results is through the Cluster Proximity Diagram
9 (CPD), which is obtained using the Silhouette Width (Beddows et al., 2009). This diagram
10 positions each cluster according to the similarity with the rest of the clusters (Figure 2e-g).
11 The closer nodes represent similar clusters, although not sufficiently alike to form a new
12 cluster. Conversely, the more distant nodes represent the most dissimilar clusters. The
13 average cluster modal diameter increases from left to right.

14 Figure 2e-g shows the corresponding CPDs for the main selected cities. The Nucleation
15 clusters NU are located in the far left side of the diagram, as they account for a very fine
16 size mode (see Table 2). Traffic clusters (T1-T3) are positioned next to NU, although their
17 location within the CPD varies depending on the city. In general, T3 and T1 are confined
18 closer to the NU clusters than T2, given their association with primary traffic emissions
19 (T1) and evaporation of traffic particles or nucleation (T3). Clusters T2 are an intermediate
20 step between fresh traffic emissions (T1) and the Urban Background clusters (UB).
21 Regarding the Background Pollution clusters (UB and SB), their location on the right side
22 of the graphs suggests that the sources/processes loading the Nucleation and Traffic
23 clusters develop and contribute to this category. Barcelona and Madrid (Figs. 2e and 2f,
24 respectively) show site specific clusters. The SB cluster in Madrid is loaded with traffic
25

1 particles from T1 and T2 before it contributes to the Nitrate (NIT) cluster. Other site
2 specific clusters such as Nitrate (NIT) are only observed in Barcelona and Madrid (Figs. 2e
3 and 2f, respectively). In the case of Barcelona, NIT is linked to the Traffic clusters T1 and
4 T2, highlighting its urban nature. On the other hand, although the Traffic clusters T2 and
5 T3 contribute to the formation of Nitrate in Madrid, both Background Pollution clusters UB
6 and SB add to its loading, thus resulting in a higher modal diameter for the NIT cluster in
7 Madrid than in Barcelona (Table 2). The remaining Growth clusters in Brisbane (G1 and
8 G2) are positioned in the centre of the CPD (Fig. 2f) and represent particle growth from NU
9 or the Traffic clusters (T1 and T3) before contributing to the UB. This is also supported by
10 their time occurrence after the NU or T clusters.

12 **4 Discussion**

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

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16 - Background pollution and Specific cases. These clusters characterise the urban
17 background and regional background pollution of the sites. They are likely composed of a
18 mixture of aerosol particle types with different sources and origins. The Urban Background
19 cluster usually describes the cleanest conditions encountered at the urban sites, ranging
20 from 6 to 22% of the time (see Table S4). The resulting average spectra for all Urban
21 Background clusters (Figure 4) show a trimodal size distribution, with two peaks in the
22 Aitken mode (at 38 ± 3 nm and 72 ± 2 nm) and a minor one in the accumulation mode at
23 168 ± 14 nm, reflecting aged aerosols mostly of an anthropogenic origin (see Table 4).
24 Specific cases were associated with "Nitrate" containing aerosol particles, and "Growth" of
25 new particle formation events. The Nitrate cluster was observed in Madrid and Barcelona.

1 whereas the Growth clusters were only seen in Brisbane. Each cluster represents around
2 10% of the time at their respective sites (see Table S4). The difference in the Nitrate size
3 distributions of Barcelona and Madrid might be due to the urban site characteristics of this
4 cluster in Barcelona, while in Madrid it is also enriched with Background clusters (see
5 Figure 2b-c). The Growth clusters reflect the size mode increase of nucleation particles
6 due to subsequent growth (see Table 2), since they are recorded after nucleation
7 episodes.

8
9 - Traffic. This category includes all clusters directly related to traffic emission sources. It
10 contains 3 subcategories (Traffic 1-Traffic 3) ranging from fresh traffic emissions to
11 aerosols that have been affected by atmospheric processes after emission, such as
12 coagulation, condensation or evaporation (Dall'Osto et al., 2011**b**). This is the dominant
13 category at all sites, showing the high prevalence of traffic emissions in the ultrafine PN
14 concentration in urban background sites. This category was found to be the main one in all
15 the studied cities, ranging from 44% in Brisbane to 63% in Barcelona (see Table 3). The
16 average Traffic size distribution shows a main peak in the Aitken mode at 31 ± 1 nm and a
17 minor one in the accumulation mode at 120 ± 2 nm (see Figure 4 and Table 4). According to
18 vehicle emission studies, the Aitken mode corresponds with grown nucleated particles
19 associated with the dilution of vehicle exhausts (Kittelson et al., 2006; Ntziachristos et al.,
20 2007), while the larger mode is associated with solid carbonaceous compounds from
21 exhausts (Shi et al., 2000; Harrison et al., 2011). The clusters included in this category are
22 characterised by the highest levels of traffic-related pollutants, such as NO, NO₂, CO and
23 BC. These values are usually higher for clusters T1 and T2 and decrease for T3 (see Fig.
24 S2).

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- Background Pollution. These clusters characterise the urban background and regional background pollution of the sites. They are likely composed of a mixture of aerosol particle types with different sources and origins. They usually describe the cleanest conditions encountered at the urban sites, ranging from 13 to 22% of the time (see Table 3). The resulting average spectra for all background clusters (Figure 4) show a trimodal size distribution, with two peaks in the Aitken mode (at 38 ± 3 nm and 72 ± 2 nm) and a minor one in the accumulation mode at 168 ± 14 nm, reflecting aged aerosols mostly of an anthropogenic origin (see Table 4). ¶
¶
- Specific case. These clusters are associated with "Nitrate" containing aerosol particles, and "Growth" of new particle formation events. The Nitrate cluster was observed in Madrid and Barcelona, whereas the Growth clusters were only seen in Brisbane. Each cluster represents around 10% of the time at their respective sites (see Table 3). The difference in 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. ¶

1 - Nucleation events. Nucleation events accounted ed for 14-19% of the hourly observations,
2 with an average of 16% of the time, indicating nucleation as an important source of UFP in
3 high insolation urban areas (see Table 3). The average Nucleation size distribution (Figure
4 4) is characterised by a high PN nucleation mode peak at 17 ± 1 nm and a lower PN peak in
5 the Aitken mode at 53 ± 7 nm (Table 4). It occurs under intense solar irradiance, clean air
6 conditions (high wind speed and low concentrations of CO, NO and NO₂), low relative
7 humidity and relatively high levels of SO₂, although still low SO₂ levels in absolute
8 concentration values (see Fig. S2). It presents the highest PN (12000 ± 8000 cm⁻³) of all
9 categories (see Figure 4). ~~In the case of Madrid, the nucleation peak coincides with a~~
10 decrease in PN at the end of the morning rush hour, while in Rome a minor peak can be
11 observed around 3 p.m., when the nucleated particles downwind of Rome reach the
12 sampling site.

13 Whilst the occurrence of an increase in PN levels related to photochemical nucleation
14 events at midday was previously discussed (Reche et al. 2011), this study allows study of
15 how new particle formation events evolve in the urban areas studied. Figure 5 shows that
16 new particle formation events in high insolation urban environments often fail to grow to
17 sizes larger than 30-40 nm (Figure 5a-c). Further growth of these nucleated particles in
18 urban environments following a banana-like shape is probably constrained by the
19 decrease in solar radiation intensity and the prevalence of traffic emitted particles in the
20 evening.

21
22 Although only three months of data are available, the same conclusion can be extracted
23 from the urban Los Angeles site, whereas aged nucleated particles downwind of Rome
24 (20-40 nm) reach the Rome regional site in the early afternoon (Fig 5d-e). Figure 6 shows
25 aerosol size distribution data collected in Barcelona, Madrid and Brisbane during the days
26 when nucleation events were detected (as k-Means cluster NU). Additionally, temperature,

Eliminado: The PN/NO_x ratio from 8 a.m. to 12 a.m. was calculated for the Nucleation and Traffic 1 clusters for each city. In all cases it was found to be higher for the Nucleation than for the Traffic 1 clusters, highlighting both the clean atmospheric conditions favouring nucleation (low NO_x levels) and the contribution of nucleated particles to PN. In summary, this study shows that new particle formation events can be an important source of UFP in urban areas under high solar radiation, as it is the dominant particle number concentration source on average for 16% of the time. This is also reflected in the average PN daily profiles, calculated using the respective SMPS total PN concentrations during the whole study period for each city (Figure S3). Indeed, in cities like Barcelona, Brisbane and Los Angeles a clear midday peak between the two rush hour peaks (morning and evening) is observed.

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Eliminado: we show that this trend is common to worldwide cities sharing a temperate climate and high solar radiation levels. Furthermore, this study shows

Eliminado: and Figure 6

Eliminado: In order to analyse this, we link our discussion to that reported in Dall'Osto et al. (2013). At least two main different types of new particle formation events can be seen in the Mediterranean urban environment:¶

¶ (1) A regional type event, originating in the whole study region and impacting almost simultaneously the city and the surrounding urban background area; ¶
¶ (2) An urban type event, which originates only within the city centre but whose growth continues while transported away from the city to the regional background.¶

¶ The main difference between these two types resides in the origin of the nucleation events (regional scale in type 1 and urban origin in type 2). Moreover, the regional events are found to start earlier in the morning than the urban type and usually display the typical banana shape implying that photochemically nucleated particles experience subsequent growth. On the other hand, the urban type nucleated particles experience less growth, reaching sizes of 30-40 nm. The city of Brisbane exhibits new particle formation events starting in the morning (see Figure 5c), similar to the regional nucleation event types discussed (... [1])

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

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

12
13 It is common in the literature to refer to the frequency of nucleation events as the
14 percentage of days such an event has been detected. The size distribution time series
15 need to be visually inspected to certify that a distinct new mode starting in the nucleation
16 range appears, that the mode prevails over some hours and that it shows signs of growth
17 (Dal Maso et al., 2005). This methodology has been proven to be very useful to detect
18 “banana-like” nucleation events, where distinct nucleation events and subsequent particle
19 growth can be observed. However, this is not the most common nucleation event type
20 detected in the studied urban environments, where an increase in the particle
21 condensation sink due to traffic emissions might constrain the growth of nucleated
22 particles. Instead, nucleation events consist of particle bursts lasting for 3-4 hours with
23 particle growth limited to 20-40 nm (see Fig. 5 and 6). Therefore, to adapt this
24 methodology to our current scenario, the percentage of days that presented nucleation
25 events were classified considering the prevalence of the Nucleation cluster from 2 up to 4
26 consecutive hours for each site. The results were found to be very homogeneous among

1 the main sampling sites (see Table 5). Nucleation events were detected for 53-58% of the
2 days lasting for two hours or more, decreasing to 37-43% for 3 hours or more and 27-30%
3 for 4 hours or more. The decrease in occurrence of long nucleation events is a
4 consequence of the limitation for nucleated particles to grow in high insolation urban
5 environments. Interrupted nucleation events were not considered, which may have led to
6 slightly higher occurrence if considered.

8 **5 Implications and Conclusions**

9
10 This study shows that traffic is a main source of UFP in the urban atmosphere, accounting
11 for 44-63% of the time. The quantified particle number concentration contribution of motor
12 vehicle emissions was also the major source in other urban locations: 47.9% in Beijing
13 (Liu et al., 2014), 69% in Barcelona (Pey et al., 2009; Dall'Osto et al., 2012), 65% in
14 London (Harrison et al., 2011; Beddows et al., 2015), 69% in Helsinki (Wegner et al.,
15 2012), 42% in Pittsburgh and 45% in Rochester (Woo et al., 2001; Stanier et al., 2004).
16 Recent source contributions of ultrafine particles in the Eastern United States also
17 identified gasoline automobiles being responsible for 40% of the ultrafine particle number
18 emissions, followed by industrial sources (33%), non-road diesel (16%), on-road diesel
19 (10%), and 1% from biomass burning and dust (Posner and Pandis, 2015). Vehicle
20 emissions consist of hot gases and primary particles, which are a highly dynamic and
21 reactive in nature mixture (Kumar et al., 2011), resulting in rapid physical and chemical
22 transformations of the emitted particles following atmospheric dilution and cooling. There
23 is a need for more field studies to map traffic related particle number concentrations and to
24 understand the particle dynamics and their dispersion in urban areas (Goel and Kumar,
25 2014).

1
2 However, the second major source of ultrafine particles in the urban atmosphere of the
3 developed urban areas herein presented is secondary aerosol formation. It is important to
4 remember that nucleation events in Northern European urban areas are found to be
5 infrequent. In the Helsinki urban atmosphere they are usually observed during noon hours
6 with a maximum during spring and autumn (Husseini et al., 2008), and overall representing
7 only about 2% of the time (Wegner et al., 2012). Additionally, these events were regional
8 because they were observed at Hyttiälä (250 km north of Helsinki). By contrast, in
9 Southern Europe, Reche et al. (2011) showed that new particle formation events do occur
10 more frequently than in Northern Europe. However, only PN was reported in that study,
11 making it harder to link aerosol sources and processes. Nonetheless, this study clearly
12 showed how new particle formation events impact the urban areas studied. In order to
13 discuss this further, we link our discussion to that reported in Dall'Osto et al. (2013). At
14 least two main different main types of new particle formation event can be seen in the
15 Mediterranean urban environment:

- 16
17 (1) A regional type event, originating over the whole study region and impacting almost
18 simultaneously the city and the surrounding urban background area;
19 (2) An urban type event, which originates only within the city centre but whose growth
20 continues while transported away from the city to the regional background.

21
22 The main difference between these two types resides in the origin of the nucleation events
23 (regional scale in type 1 and urban origin in type 2). Moreover, the regional events are
24 found to start earlier in the morning than the urban type and usually display the typical
25 banana shape implying that photochemically nucleated particles experience subsequent

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

1 growth. On the other hand, the urban type nucleated particles experience less growth,
2 reaching sizes of 30-40 nm, as clearly shown in Fig. 6.

3 The city of Brisbane exhibits new particle formation events starting in the morning (see
4 Figure 5c), similar to the regional nucleation event types discussed in Dall'Osto et al.
5 (2013) as they are often followed by particle growth showing a banana-shape (Cheung et
6 al., 2011). This may be due to the fact that the Brisbane site is located in a relatively clean
7 environment. By contrast we find that the majority of new particle formation events
8 detected in the other cities occur under the highest solar irradiance and thus around noon.
9 Such events are characterised by a burst of particles lasting for about 3-4 h (Figure 5, 6),
10 as reported in Dall'Osto et al. (2013).

11
12 It should be noted that many urban areas exposed to high insolation are also
13 characterised by high condensation sinks. This is the case of many developing urban
14 areas, where new particle formation events are limited. For example, particle bursts in the
15 nucleation mode size range (5-25 nm), followed by a sustained growth in size were
16 observed very rarely (only 5 out of 79 observation days) in a tropical Southern India site,
17 less frequently than at most other locations around the world during May-July (Kanawade
18 et al., 2014a). New particle formation at two distinct Indian sub-continental urban locations
19 were observed with lower frequency at Kampur (14%) than that at Pune (26%), due to the
20 presence of pre-existing large particles at the former site (Kanawade et al., 2014b).
21 Observations of new aerosol particle formation in a tropical urban atmosphere (Betha et
22 al., 2013) were also found to be suppressed by very high pre-existing particle
23 concentrations during haze periods (Betha et al., 2014). Zhu et al. (2014) reported fewer
24 new particle formation events in a severely polluted atmosphere (Qingdao, China) than in
25 Toronto (Canada). Long-term measurements of particle number size distributions in urban
26 Beijing and in the North China Plain showed homogeneous nucleation events

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

1 characterized by the co-existence of a stronger source of precursor gases and a higher
2 condensational sink of pre-existing aerosol particles than European cities (Wang et al.,
3 2013a, b).
4 Regional nucleation can be seen in urban areas more frequently over the weekend
5 (Sabaliauskas et al., 2013). Ragetti et al. (2014) recently reported spatio-temporal
6 variation of urban ultrafine particle number concentrations, showing that the most
7 important predictor for all models was the suburban background UFP concentration,
8 explaining 50% and 38% of the variability of the median and mean, respectively.
9 Frequencies of new particle formation (NPF) events in China were much higher at urban
10 and regional sites than at coastal sites and during open ocean cruise measurement (Peng
11 et al., 2014).

12 ▾
13 This has important implications because the city seems to be not only a source of primary
14 UFP but also a driver for nucleation events occurring only in the city. Little is known about
15 health effects of UFP in urban areas (HEI Overview Panel, 2013), the possible
16 mechanisms and chemical components responsible for such events, or if there are
17 differences in health impact between the two nucleation event types discussed here. Given
18 that we are still in the early stages of our understanding of the toxicology and epidemiology
19 of urban UFP, adoption of the precautionary principle in attempting to reduce such
20 emissions would seem wise. The urban nucleation events described in this paper
21 presumably have an anthropogenic origin, or at least are influenced by anthropogenic
22 precursors, due to the fact that such events are seen initiating in city hot spots and not in
23 the nearby background (Dall'Osto et al., 2013). On average, nucleation events lasting for
24 two hours or more were detected in 55% of the days, this extending to over four hours in
25 28% of the days, demonstrating that the atmospheric conditions in urban environments do
26 not favour photochemically nucleated particle growth. Traffic remains a major source of

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The urban nucleation events described in this paper presumably have an anthropogenic origin, or at least be influenced by anthropogenic precursors, due to the fact that such events are seen initiating in city hot spots and not in the nearby background (Dall'Osto et al., 2013). Betha et al. (2013) reached the same conclusion regarding urban nucleation episodes in a tropical environment (Singapore).

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Eliminado: 5 Conclusions¶
With the aim of evaluating the nature and impact of urban nucleation events on levels of ambient UFP in high insolation urban environments, we apply a unified specialized tool to long term data sets (1-2 years) sampled at several cities. Size resolved particle measurements were performed in three urban background environments in high insolation regions: Barcelona, Madrid and Brisbane. Measurements from Rome and Los Angeles were also included to complement the study. Individual studies have demonstrated the occurrence of urban nucleation events in certain cities; however this is the first study that systematically assesses such events in worldwide cities with a similar climate. To this end a k-Means clustering analysis was performed on each data set, summarised in four main categories: "Traffic", "Background Pollution", "Nucleation" and "Specific case". Although the main source of UFP was attributed to road traffic emissions (representing 44-63% of the time), photochemical nucleation events accounted on average for 16% of the observations, being a relevant source of UFP in high insolation urban environments. This is reflected in the midday peak of daily average PN levels recorded at many of the study cities due to nucleation events, although most of these events were not followed by growth, with most of the detected events lasting about 1-4 hours and reaching sizes of about 30-40 nm. At least two different new particle formation events were classified: one starting in the morning at about 9-12 a.m., and a second one starting in the afternoon at about 1-4 p.m. (Dall'Osto et al., 2013). Both events did not last more than 3-6 hours, indicating the urban environment is not one that allows full growth of particles as seen in the more remote regional background.

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

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24 manuscript.

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1 **6 References**

2
3 Alam, A., Shi, J.P. and Harrison, R.M.: Observations of new particle formation in urban air,
4 J. Geophys. Res., 108 (D3), 4093, doi: 10.1029/2001JD001417, 2003.

5
6
7 Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M. and Armstrong, B.: Urban
8 particle metrics and health: A time series analysis, Epidemiology, 21, 501-511, 2010.

9 Australian Bureau of Statistics, 2014: <http://www.abs.gov.au/ausstats/abs@.nsf/mf/9309.0>

10
11 Beddows, D.C.S., Dall'Osto, M. and Harrison, R.M.: Cluster analysis of rural, urban and
12 curbside atmospheric particle size data, Environ. Sci. Technol., 43, 4694-4700, 2009.

13
14 [Beddows, D. C. S., Dall'Osto, M., Harrison, R. M., Kulmala, M., Asmi, A., Wiedensohler,](#)
15 [A., Laj, P., Fjaeraa, A.M., Sellegri, K., Birmili, W., Bukowiecki, N., Weingartner, E.,](#)
16 [Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J.-P., Marinoni, A., Tunved, P.,](#)
17 [Hansson, H.-C., Fiebig, M., Kivekäs, N., Swietlicki, E., Lihavainen, H., Asmi, E., Ulevicius,](#)
18 [V., Aalto, P. P., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., de Leeuw, G.,](#)
19 [Henzing, B., O'Dowd, C., Jennings, S. G., Flentje, H., Meinhardt, F., Ries, L., Denier van](#)
20 [der Gon, H. A. C., and Visschedijk, A. J. H.: Variations in tropospheric submicron particle](#)
21 [size distributions across the European continent 2008–2009, Atmos. Chem. Phys., 14,](#)
22 [4327-4348, doi:10.5194/acp-14-4327-2014, 2014.](#)

23
24 [Beddows, D. C. S., Harrison, R. M., Green, D. C.. and Fuller, G. W.: Receptor modelling of](#)
25 [both particle composition and size distribution from a background site in London, UK,](#)
26 [Atmos. Chem. Phys. Discuss., 15, 10123-10162, doi:10.5194/acpd-15-10123-2015, 2015.](#)

27
28 Betha, R., Spracklen, D.V., Balasubramanian, R.: Observations of new aerosol particle
29 formation in a tropical urban atmosphere, Atmos. Environ., 71, 340-351, 2013.

Con formato: Fuente de párrafo predeter., Fuente: (Predeterminado) Arial, Inglés (Reino Unido)

Con formato: Fuente de párrafo predeter., Fuente: (Predeterminado) Arial, Color de fuente: Negro, Inglés (Reino Unido)

1 [Betha, R., Zhang, Z. and Balasubramanian, R.: Influence of trans-boundary biomass](#)
2 [burning impacted air masses on submicron number concentrations and size distributions,](#)
3 [Atmos. Environ. 92, 9-18, 2014.](#)

4
5 von Bismarck-Osten, C., Birmili, W., Ketzel, M., Massling, A., Petäjä, T., Weber, S.:
6 Characterization of parameters influencing the spatio-temporal variability of urban particle
7 number size distributions in four European cities, *Atmos. Environ.*, 77, 415-429, 2013.

8
9 Boy, M. and Kulmala, M.: Nucleation events in the continental boundary layer: Influence of
10 the physical and meteorological parameters, *Atmos. Chem. Phys.*, 2, 1-16, 2002.

11
12 Brines, M., Dall'Osto, M., Beddows, D.C.S., Harrison, R. M., and Querol, X.: Simplifying
13 aerosol size distributions modes simultaneously detected at four monitoring sites during
14 SAPUSS, *Atmos. Chem. Phys.*, 14, 2973-2986, doi:10.5194/acp-14-2973-2014, 2014.

15
16 Buonanno, G. and Morawska, L.: Ultrafine particle emission of waste incinerators and
17 comparison to the exposure of urban citizens, *Waste Manage.*, 37, 75-81, 2015.

18
19 Charron, A. and Harrison, R. M.: Primary particle formation from vehicle emissions during
20 exhaust dilution in the roadside atmosphere, *Atmos. Environ.*, 37, 4109–4119, 2003.

21
22 Cheung, H.C., Morawska, L. and Ristovski, Z.D.: Observation of new particle formation in
23 subtropical urban environment, *Atmos. Chem. Phys.*, 11, 3823-3833, 2011.

24
25 Cheung, H. C., Chou, C. C.-K., Huang, W.-R., and Tsai, C.-Y.: Characterization of ultrafine
26 particle number concentration and new particle formation in an urban environment of
27 Taipei, Taiwan, *Atmos. Chem. Phys.*, 13, 8935-8946, doi:10.5194/acp-13-8935-2013,
28 2013.

29

1 Ciccioni, P., Brancaleoni, E., Frattoni, M.: Reactive hydrocarbons in the atmosphere at
2 urban and regional scale, Hewitt, N.C., Reactive Hydrocarbons in the Atmosphere,
3 Academic Press, 159-207, 1999.

4
5 [Colbeck, I., Lazaridis, M.: Aerosol Science: technology and Application. First Edition ©
6 2014 John Wiley & Sons, Ltd. ISBN: 978-1-119-97792-6.](#)

7
8 Costabile, F., Birmili, W., Klose, S., Tuch, T., Wehner, B., Wiedensohler, A., Franck, U.,
9 König, K., and Sonntag, A.: Spatio-temporal variability and principal components of the
10 particle number size distribution in an urban atmosphere, Atmos. Chem. Phys., 9, 3163-
11 3195, doi:10.5194/acp-9-3163-2009, 2009.

12
13 Costabile, F., Amoroso, A. and Wang, F.: Sub- μm particle size distributions in a suburban
14 Mediterranean area. Aerosol populations and their possible relationship with HONO mixing
15 ratios, Atmos. Environ., 44, 5258-5268, 2010.

16
17 Dall'Osto, M., Monahan, C., Greaney, R., Beddows, D. C. S., Harrison, R. M., Ceburnis,
18 D., and O'Dowd, C. D.: A statistical analysis of North East Atlantic (submicron) aerosol
19 size distributions, Atmos. Chem. Phys., 11, 12567-12578, doi:10.5194/acp-11-12567-
20 2011, 2011a.

21
22 Dall'Osto, M., Thorpe, A., Beddows, D. C. S., Harrison, R. M., Barlow, J. F., Dunbar, T.,
23 Williams, P. I., and Coe, H.: Remarkable dynamics of nanoparticles in the urban
24 atmosphere, Atmos. Chem. Phys., 11, 6623–6637, 2011b.

25
26 Dall'Osto, M., Beddows, D.C.S., Pey, J., Rodriguez, S., Alastuey, A., Harrison, R. M. and
27 X. Querol: Urban aerosol size distributions over the Mediterranean city of Barcelona, NE
28 Spain, Atmos. Chem. Phys., 12, 10693-10707, doi:10.5194/acp-12-10693-2012, 2012.

29

Eliminado: ¶

1 Dall'Osto, M., Querol, X., Alastuey, A., O'Dowd, C., Harrison, R.M., Wenger, J. and
2 Gómez Moreno, F.J.: On the spatial distribution and evolution of ultrafine particles in
3 Barcelona, Atmos. Chem. Phys., 13, 741-759, doi:10.5194/acp-13-741-2013, 2013.
4
5 Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P. and Lehtinen,
6 K. E. J.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size
7 distribution data from SMEAR II, Hyytiälä, Finland. Boreal Env. Res., 10: 323–336, 2005.
8
9 Dirección General de Tráfico (DGT), 2015.
10 <https://sedeapl.dgt.gob.es/IEST2/menu.do?path=/vehiculos/parque/&file=inebase&type=pc>
11 [axis&L=0&js=1](https://sedeapl.dgt.gob.es/IEST2/menu.do?path=/vehiculos/parque/&file=inebase&type=pc)
12
13 [Duyzer, J., van der Hout, D., Zandveld, P. and van Ratingen, S: Representativeness of air](#)
14 [quality monitoring networks. Atmos. Environ., 104, 88-101, 2015.](#)
15
16 [EU, 2012. Commissions Regulation \(EU\) No. 459/2012. Official Journal of the European](#)
17 [Union. <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32012R0459> \(accessed](#)
18 [on 08 Apr 2014\).](#)
19
20 [Goel, A. and Kumar, P.: A review of fundamental drivers governing the emissions,](#)
21 [dispersion and exposure to vehicle-emitted nanoparticles at signalised traffic intersections,](#)
22 [Atmos. Environ. 97, 316-331, 2014.](#)
23
24 Gómez-Moreno, F.J., Núñez, L., Plaza, J., Alonso, D., Pujadas, M. and Artíñano, B.:
25 Annual evolution and generation mechanisms of particulate nitrate in Madrid, Atmos.
26 Environ, 41, 394-406, 2007.
27
28 Gómez-Moreno, F.J., Pujadas, M., Plaza, J., Rodríguez-Maroto, J.J., Martínez-Lozano, P.,
29 Artíñano, B.: Influence of seasonal factors on the atmospheric particle number
30 concentration and size distribution in Madrid, Atmos. Environ., 45, 3199-3180, 2011.

1

2 Harris, S. J. and Maricq, M. M.: Signature size distributions for diesel and gasoline engine
3 exhaust particulate matter, *J. Aerosol Sci.*, 32, 749–764, 2001.

4

5 Harrison, R.M., Beddows, D.C.S. and Dall’Osto M.: PMF analysis of wide-range particle
6 size spectra collected on a major highway, *Environ. Sci. Technol.*, 45, 5522-5528, 2011.

7

8 HEI Review Panel on Ultrafine Particles, Understanding the Health Effects of Ambient
9 Ultrafine Particles, HEI Perspectives 3, Health Effects Institute, Boston, MA. 2013.

10

11 [Huang, L., Gong, S. L., Gordon, M., Liggio, J., Staebler, R., Stroud, C. A., Lu, G., Mihele,](#)
12 [C., Brook, J. R., and Jia, C. Q.: Aerosol–computational fluid dynamics modeling of ultrafine](#)
13 [and black carbon particle emission, dilution, and growth near roadways, *Atmos. Chem.*](#)
14 [Phys., 14, 12631-12648, doi:10.5194/acp-14-12631-2014, 2014.](#)

15

16 Hudda, N., Cheung, K., Moore, K.F. and Sioutas, C.: Inter-community variability in total
17 particle number concentrations in the eastern Los Angeles air basin, *Atmos. Chem. Phys.*,
18 10, 11385-11399, 2010.

19

20 [Hussein, T., Martikainen, J., Junninen, H., Sogacheva, L., Wagner, R., Maso, M.D.,](#)
21 [Riiipinen, I., Aalto, P.P., Kulmala, M.: Observation of regional new particle formation in the](#)
22 [urban atmosphere, *Tellus B*, 60, 509-521, 2008.](#)

23

24 [Hussein, T., Molgaard, B., Hannuniemi, H., Martikainen, J., Järvi, L., Wegner, T.,](#)
25 [Ripamonti, G., Weber, S., Vesala, T. and Hämeri, K.: Fingerprints of the urban particle](#)
26 [number size distribution in Helsinki, Finland: Local versus regional characteristics, *Boreal*](#)
27 [Env. Res.](#), 19, 1-20, 2014.

28

1 Istituto Nazionali di Statistica, 2009: Annuari di Statistiche Ambientali 2009, n.11-2009,
2 http://www3.istat.it/dati/catalogo/20091130_00/ann_09_11statistich_%20ambientali09.pdf

3

4 [Kanawade, V. P., Shika, S., Pöhlker, C., rose, D., Suman, M.N.S., Gadhavi, H., Kumar, A.,](#)
5 [Shiva Nagendra, S.M., Ravikrishna, R., Yu, H., Sahu, L.K., Jayaraman, A., Andreae, M.O.,](#)
6 [Pöschl, U. and Gunthe, S.S: Infrequent occurrence of new particle formation at a semi-](#)
7 [rural location, Gadanki, in tropical Southern India, Atmos. Environ., 94, 264-273, 2014a.](#)

8

9 [Kanawade, V.P., Tripathi, S.N., Siingh, D., Gautam, A.S., Srivastava, A.K., Kamra, A.K.,](#)
10 [Soni, V.K. and Sethi, V.: Observations of new particle formation at two distinct Indian](#)
11 [subcontinental urban locations, Atmos. Environ., 96, 370-379, 2014b.](#)

12

13 Kittelson, D.B.: Engines and nanoparticles: a review, J. Aerosol Sci. 29, 5/6, 575-588,
14 1998.

15

16 Kittelson, D.B., Watts, W.F., Johnson, J.P.: On-road and laboratory evaluation of
17 combustion aerosols-Part1: Summary of diesel engine results, J. Aerosol Sci., 37, 913-
18 930, 2006.

19

20 Kulmala M., Vehkamehk H., Pet, P T., Dal Maso M., Lauri A., Kerminen V.-M., Birmili W.
21 and McMurry P.: Formation and growth rates of ultrafine atmospheric particles: a review of
22 observations, J. Aerosol Sci., 35, 143afin, 2004.

23

24 Kulmala, M. and Kerminen, V.M.: On the formation and growth of atmospheric
25 nanoparticles, Atmos. Research, 90, 132-150, 2008.

26

27 Kumar, P., Ketzel, M., Vardoulakis, S., Pirjola, L., Britter, R.: Dynamics and dispersion
28 modelling of nanoparticles from road traffic in the urban atmospheric environment -A
29 review. J. Aerosol Sci. 42, 580-603, 2011.

30

1 [Kumar, P., Morawska, L., Birmili, W., Paasonen, P., Hu, M., Kulmala, M., Harrison, R.M.,](#)
2 [Norford, L. and Britter, R.: Ultrafine particles in cities, Environ. Int., 66, 1-10, 2014.](#)
3
4 Laaksonen, A., Hamed, A., Joutsensaari, J., Hiltunen, L., Cavalli, F., Junkermann, W.,
5 Asmi, A., Fuzzi, S. and Facchini, M. C.: Cloud condensation nucleus production from
6 nucleation events at a highly polluted region, Geophys. Res. Lett., 32, L06812,
7 doi:[10.1029/2004GL022092](#), 2005.
8
9 [Liu, Z.R., Hu, B., Liu, Q., Sun, Y., Wang, Y.S.: Source apportionment of urban fine particle](#)
10 [number concentration during summertime in Beijing, Atmos. Environ., 95, 359-369, 2014.](#)
11
12 Ntziachristos, L., Ning, Z., Geller, M. D., and Sioutas, C.: Particle concentration and
13 characteristics near a major freeway with heavy-duty diesel traffic, Environ. Sci. Technol.,
14 41, 2223–2230, 2007.
15
16 O’Dowd, C., Monahan, C., and Dall’Osto, M.: On the occurrence of open ocean particle
17 production and growth events, Geophys. Res. Lett., 37, L19805,
18 doi:[10.1029/2010GL044679](#), 2010.
19
20 Oberdorster, G., Oberdorster, E. and Oberdorster, J.: Nanotoxicology: An emerging
21 discipline evolving from studies of ultrafine particles, Environmental Health Perspectives,
22 113, 7, 823-839, 2005.
23
24 [Peng, J. F., Hu, M., Wang, Z. B., Huang, X. F., Kumar, P., Wu, Z. J., Guo, S., Yue, D. L.,](#)
25 [Shang, D. J., Zheng, Z., and He, L. Y.: Submicron aerosols at thirteen diversified sites in](#)
26 [China: size distribution, new particle formation and corresponding contribution to cloud](#)
27 [condensation nuclei production, Atmos. Chem. Phys., 14, 10249-10265, doi:\[10.5194/acp-\]\(#\)](#)
28 [14-10249-2014, 2014.](#)
29

1 [Peters, J., Van der Bossche, J., Reggente, M., Van Poppel, M., de Baets, B., Theunis, J.:](#)
2 [Cyclist exposure to UFP and BC on urban routes in Antwerp, Belgium, Atmos. Environ. 92,](#)
3 [31-43, 2014.](#)
4
5 Pey, J., Rodríguez, S., Querol, X., Alastuey, A., Moreno, T., Putaud, J. P., and Van
6 Dingenen, R.: Variations of urban aerosols in the western Mediterranean, Atmos. Environ.,
7 42, 9052–9062, 2008.
8
9 Pey, J., Querol, X., Alastuey, A., Rodríguez, S., Putaud, J. P., and Van Dingenen, R.:
10 Source Apportionment of urban fine and ultrafine particle number concentration in a
11 Western Mediterranean city, Atmos. Environ., 43, 4407–4415, 2009.
12
13 [Posner, L. N. and Pandis, S. N.: Sources of ultrafine particles in the Eastern United States,](#)
14 [Atmos. Environ., 111, 103-112, 2015.](#)
15
16 [Ragetti, M.S., Ducret-Stich, R.E., Foraster, M., Morelli, X., Aguilera, I., Basagaña, X.,](#)
17 [Corradi, E., Ineichen, A., Tsai, M.-Y., Probst-Hensch, N., Rivera, M., Slama, R., Künzli, N.](#)
18 [and Phuleria, H.C.: Spatio-temporal variation of urban ultrafine particle number](#)
19 [concentrations : Spatio-temporal variation of urban ultrafine particle number concentration,](#)
20 [Atmos. Environ.,96, 275-283, 2014.](#)
21
22 Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodríguez, S.,
23 González, Y., Fernández - Camacho, R., de la Rosa, J., Dall'Osto, M., Prévôt, A. S. H.,
24 Hueglin, C., Harrison, R. M., and Quincey, P.: New considerations for PM, Black Carbon
25 and particle number concentration for air quality monitoring across different European
26 cities, Atmos. Chem. Phys., 11, 6207–6227, 2011.
27
28 Revuelta, M.A., Harrison, R.M., Núñez, L., Gómez-Moreno, F.J., Pujadas, M. and
29 Artíñano, B.: Comparison of temporal features of sulphate and nitrate at urban and rural
30 sites in Spain and the UK, Atmos. Environ., 60, 383-391, 2012.
31

1 Rimnácová, D., Zdimal, V., Schwarz, J., Smolík, J. and Rimnác, M.: Atmospheric aerosols
2 in suburb of Prague: The dynamics of particle size distributions, *Atmos. Research*, 101,
3 539-552, 2011.

4

5 [Ruths, M., von Bismarck-Osten, C. and Weber, C.: Measuring and modelling the local-
6 scale spatio-temporal variation of urban particle number size distributions and black
7 carbon, *Atmos. Environ.*, 96, 37-49, 2014.](#)

8 Sabaliauskas, K., Jeong, C.-H., Yao, X., Jun, Y.-S. and Evans, G.: Cluster analysis of
9 roadside ultrafine particle size distributions, *Atmos. Environ.*, 70, 64-74, 2013.

10

11 Salimi, F., Ristovski, Z., Mazaheri, M., Laiman, R., Crilley, L.R., He, C., Clifford, S. and
12 Morawska, L.: Assessment and application of clustering techniques to atmospheric particle
13 number size distribution for the purpose of source apportionment, *Atmos. Chem. Phys.*
14 *Discuss.*, 14, 15257-15281, doi:10.5194/acpd-14-15257-2014, 2014.

15

16 Salma, I., Borsós, T., Aalto, P., Hussein, T., Dal Maso, M. and Kulmala, M.: Production,
17 growth and properties of ultrafine atmospheric aerosol particles in an urban environment,
18 *Atmos. Chem. Phys.*, 11, 1339-1353, 2011.

19

20 [Salma, I., Fűri, P., Németh, Z., Balásházy, I., Hofmann, W. and Farkas, A.: Lung burden
21 and deposition distribution of inhaled atmospheric urban ultrafine particles as the first step
22 in their health risk assessment, *Atmos. Environ.* 104, 39-49, 2015.](#)

23

24 Sellegri, K., Laj, P., Venzac, H., Boulon, J., Picard, D., Villani, P., Bonasoni, P.,
25 Marinoni, A., Cristofanelli, P., and Vuillermoz, E.: Seasonal variations of aerosol size
26 distributions based on long-term measurements at the high altitude Himalayan site of
27 Nepal Climate Observatory-Pyramid (5079 m), Nepal, *Atmos. Chem. Phys.*, 10, 10679-
28 10690, doi:10.5194/acp-10-10679-2010, 2010.

29

30 Shi, J. P. and Harrison, R. M.: Investigation of ultrafine particle formation during diesel
31 exhaust dilution, *Environ. Sci. Technol.*, 33, 3730–3736, 1999.

Eliminado: ¶

1
2 Shi, J. P., Mark, D., and Harrison, R. M.: Characterization of particles from a current
3 technology heavy-duty diesel engine, *Environ. Sci. Technol.*, 34, 748–755, 2000.
4
5 Stanier, C.O., Khlystov, A.Y. and Pandis, S.N.: Nucleation events during the Pittsburgh air
6 quality study: description and relation to key meteorological, gas phase, and aerosol
7 parameters, *Aerosol Sci. Tech.*, 38 (S1):253-264, 2004.
8
9 [Swietlicki, E., Hansson, H.-C., Hämeri, K., Svenningsson, B., Massling, A., McFinnigans,](#)
10 [G., McMurray, P.H., Petäjä, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E.,](#)
11 [Baltensperger, U., Rissler, J., Wiedensohler, A. and Kulmala, M.: Hygroscopic properties](#)
12 [of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in](#)
13 [various environments-a review, *Tellus*, 60B, 432-469, 2008.](#)
14
15 [Uhrner, U., von Louis, S., Vehkamäki, H., Wehner, B., Brasel, S., Hermann, M.,](#)
16 [Stratmann, F., Kulmala, M. and Wiedensohler, A.: Dilution and aerosol dynamics within a](#)
17 [diesel car exhaust plume – CFD simulations of on-road conditions, *Atmos. Environ.*, 41,](#)
18 [7440–7461, 2007.](#)
19
20 [Väänänen, R., Kyrö, E.-M., Nieminen, T., Kivekäs, N., Junninen, H., Virkkula, A., Dal](#)
21 [Maso, M., Lihavainen, H., Viisanen, Y., Svenningsson, B., Holst, T., Arneth, A., Aalto, P.](#)
22 [P., Kulmala, M., and Kerminen, V.-M.: Analysis of particle size distribution changes](#)
23 [between three measurement sites in northern Scandinavia, *Atmos. Chem. Phys.*, 13,](#)
24 [11887-11903, doi:10.5194/acp-13-11887-2013, 2013.](#)
25
26 Vakkari, V., Laakso, H., Kulmala, M., Laaksonen, A., Mabaso, D., Molefe, M., Kgabi, N.,
27 and Laakso, L.: New particle formation events in semi-clean South African savannah,
28 *Atmos. Chem. Phys.*, 11, 3333-3346, doi:10.5194/acp-11-3333-2011, 2011.
29
30 [Wang, Z. B., Hu, M., Sun, J. Y., Wu, Z. J., Yue, D. L., Shen, X. J., Zhang, Y. M., Pei, X. Y.,](#)
31 [Cheng, Y. F., and Wiedensohler, A.: Characteristics of regional new particle formation in](#)

Eliminado: ¶

1 [urban and regional background environments in the North China Plain, Atmos. Chem.](#)
2 [Phys., 13, 12495-12506, doi:10.5194/acp-13-12495-2013, 2013a.](#)
3
4 [Wang, Z. B., Hu, M., Wu, Z. J., Yue, D. L., He, L. Y., Huang, X. F., Liu, X. G., and](#)
5 [Wiedensohler, A.: Long-term measurements of particle number size distributions and the](#)
6 [relationships with air mass history and source apportionment in the summer of Beijing,](#)
7 [Atmos. Chem. Phys., 13, 10159-10170, doi:10.5194/acp-13-10159-2013, 2013b.](#)
8
9 [Wegner, T., Hussein, T., Hämeri, K., Vesala, T., Kulmala, M., Weber, S.: Properties of](#)
10 [aerosol signature size distributions in the urban environment as derived by cluster](#)
11 [analysis, Atmos. Environ., 61, 350-360, 2012.](#)
12
13 [Wehner, B., Siebert, H., stratman, F., Tuch, T., Wiedensohler, A., Petäjä, T., dal Maso, M.](#)
14 [and Kulmala, M.: Horizontal homogeneity and vertical extent of new particle formation](#)
15 [events, Tellus, 59B, 362-371, 2007.](#)
16
17 [Wehner, B., Uhrner, U., von Löwis, S., Zallinger, M., Wiedensohler, A: Aerosol Number](#)
18 [Size Distributions within the Exhaust Plume of a Diesel and a Gasoline Passenger Car](#)
19 [under On-Road Conditions and Determination of Emission Factors, Atmos. Environ., 43,](#)
20 [1235-1245, 2009.](#)
21
22 Wiedensohler, A., Wehner, B., Birmili, W.: Aerosol number concentrations and size
23 distributions at mountain-rural, urban-influenced rural, and urban-background sites in
24 Germany, Journal of Aerosol Medicine-Deposition Clearance and Effects in the Lung, 15
25 (2), 237–243, 2002.
26
27 Woo, K.S., Chen, D.R., Pui, D.Y.H and McMurry, P.H.: Measurement of Atlanta aerosol
28 size distributions: observations of ultrafine particle events, Aerosol Sci. Tech., 34, 75-87,
29 2001.
30

1 [Wu, Z., Hu, M., Liu, S., Wehner, B. and Wiedensohler, A.: Particle number size distribution](#)
2 [in the urban atmosphere of Beijing, China, Atmos. Environ., 42, 7967-7980, 2008.](#)

3
4 [Zhu, Y., Hinds, W.C., Kim, S. and Sioutas, C.: Concentration and size distribution of](#)
5 [ultrafine particles near a major highway, Journal of the air & waste management](#)
6 [association, 52\(9\), 1032-1042, 2002.](#)

7
8 [Zhu, Y., Sabaliauskas, K., Liu, X., Meng, H., Gao, H., Jeong, C.-H., Evans, G.J. and Yao,](#)
9 [X.: Comparative analysis of new particle formation events in less and severely polluted](#)
10 [urban atmosphere, Atmos. Environ., 98, 655-664, 2014.](#)

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13 TABLE LEGENDS

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

17
18 **Table 2:** Log-Normal fitting peaks for each cluster category *k*-Means size distribution at
19 the main sites and the corresponding peak area percentage.

20
21 **Table 3:** Cluster categories (Traffic, Nucleation, Background and Specific case (SC)) and
22 their occurrence at the main sites.

23
24 **Table 4:** *k*-Means cluster categories average size distribution size mode peaks and
25 corresponding area percentage. Only the main cities BCN, MAD and BNE were
26 considered.

27
28 **Table 5:** Percentage of nucleation event days at the main cities BCN, MAD and BNE, and
29 the uninterrupted time prevalence of these events.

30 31 FIGURE LEGENDS

1

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

8

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

15

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

21

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

25

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

31

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

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

* Australian Government Bureau of Meteorology

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

[§] National Oceanic and Atmospheric Administration (NOAA)

⁺ National Aeronautics and Space Administration (NASA)

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%)

1

2

3 **Table 3:** Cluster categories (Traffic, Nucleation, Background and Specific case (SC)) and
4 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%

1

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

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

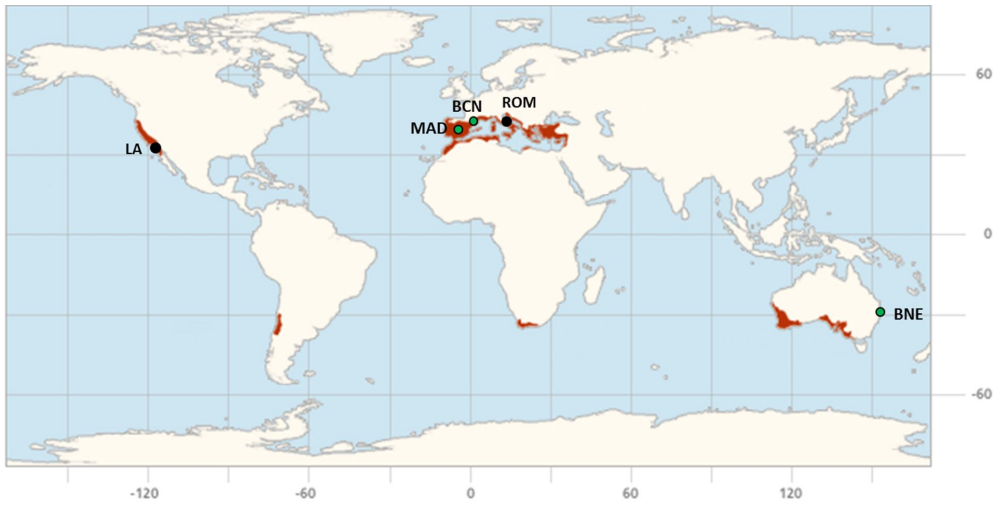
City	2 h or more	3 h or more	4 h or more
Barcelona	54%	43%	28%
Madrid	58%	41%	30%
Brisbane	53%	37%	27%

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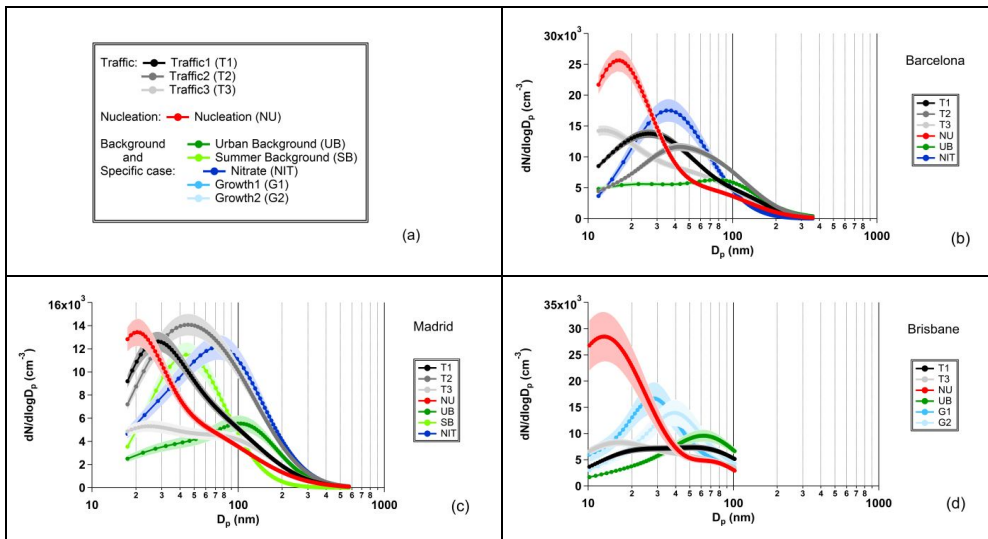
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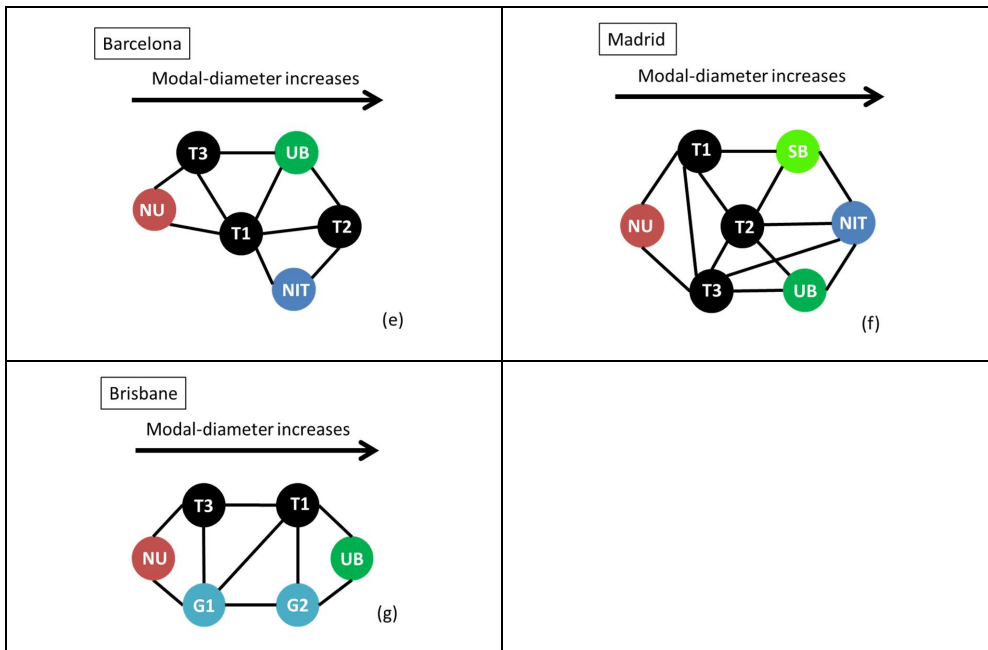


■ Mediterranean climate areas

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

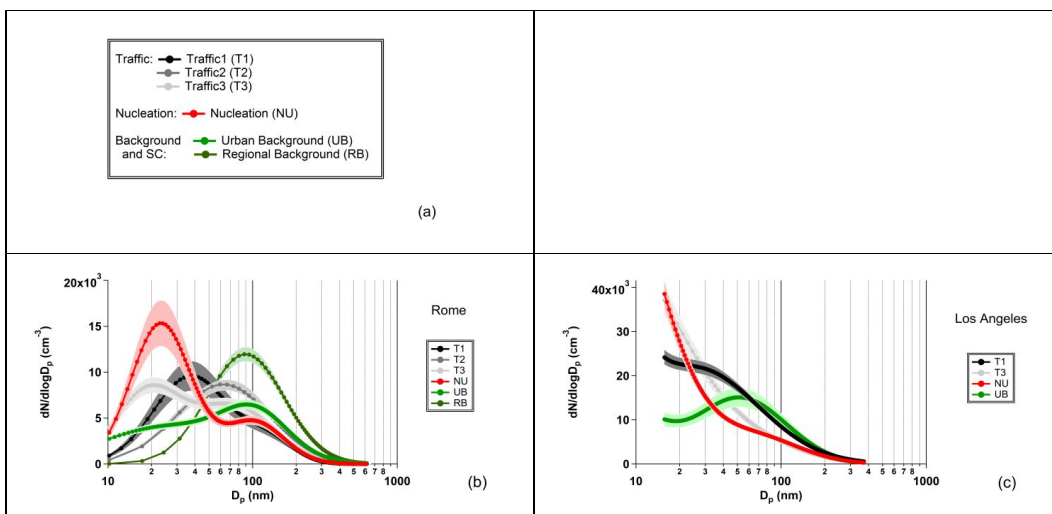
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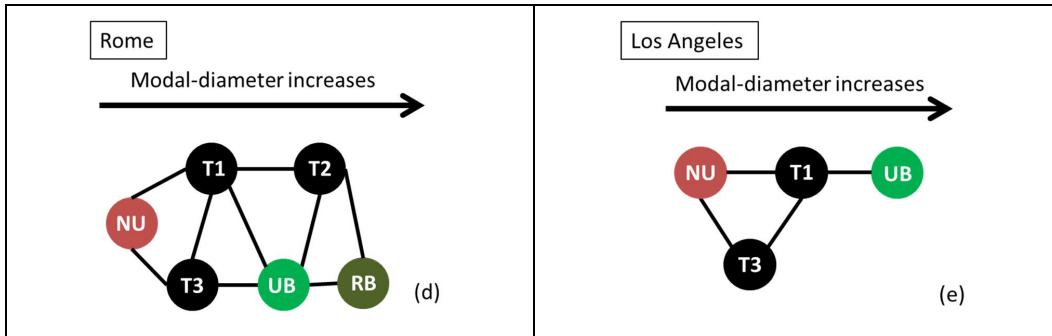




1 **Figure 2:** Aerosol size distribution results of the *k*-Means cluster analysis performed on
 2 the SMPS data at each selected city: a) legend, b) Barcelona, c) Madrid, d) Brisbane.
 3 Shaded areas around the curves represent the confidence limits μ calculated for 99.9%
 4 confidence level. Please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

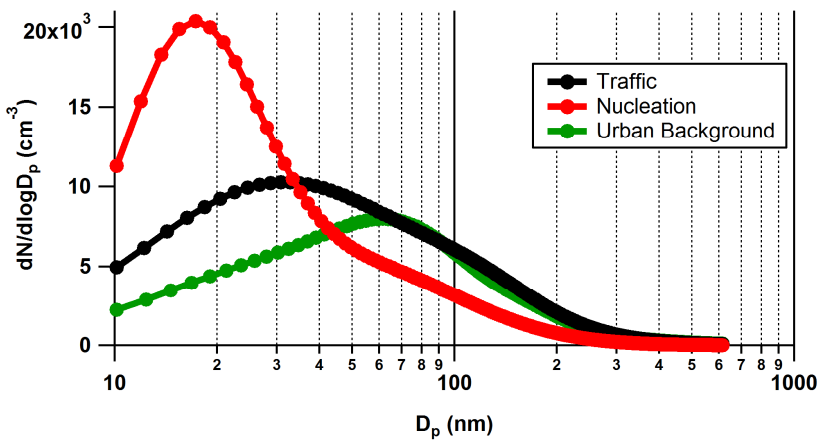
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1 **Figure 3:** Aerosol size distribution results of the *k*-Means cluster analysis performed on
 2 the SMPS data at the selected complementary cities: a) legend, b) Rome and c) Los
 3 Angeles. Shaded areas around the curves represent the confidence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

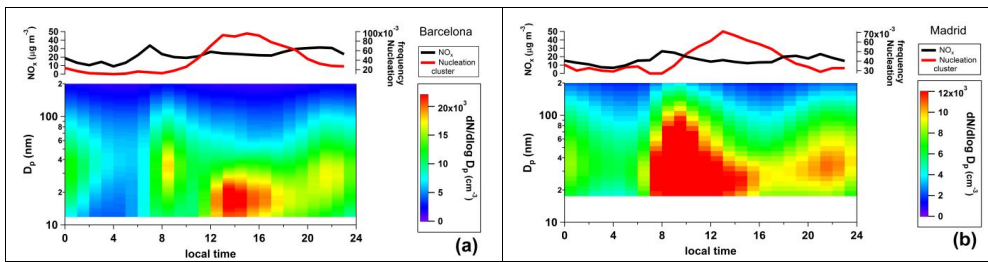
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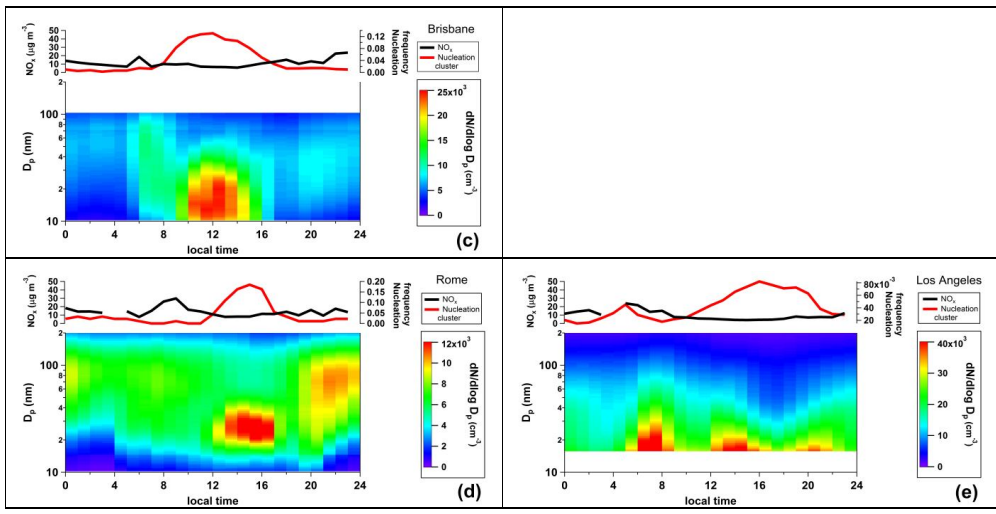


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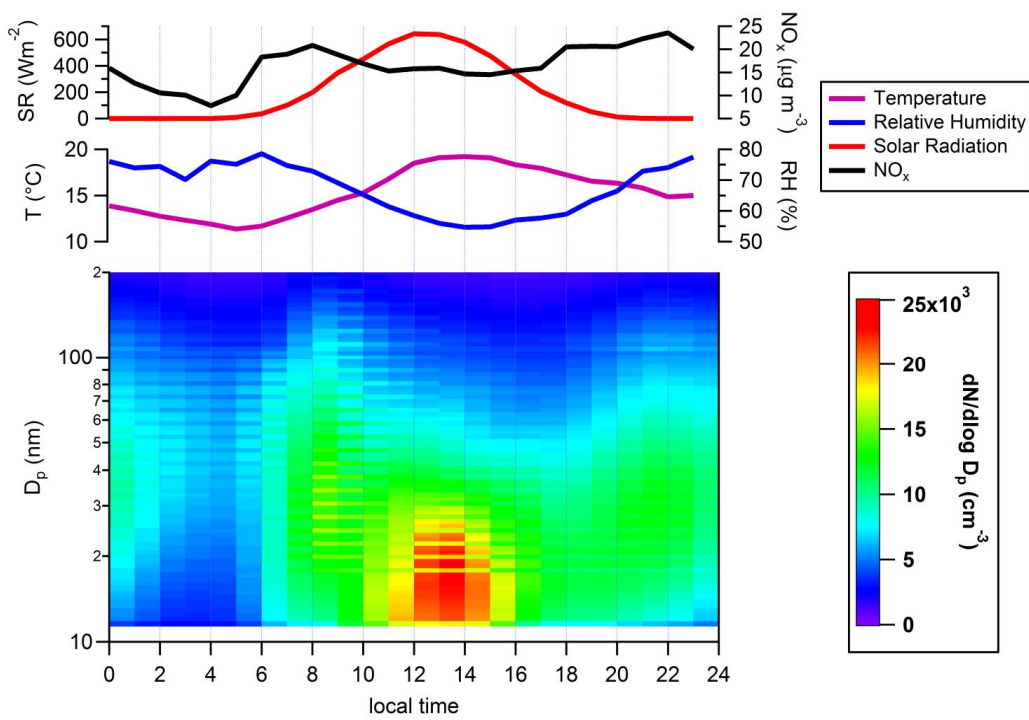
1 **Figure 4:** Average aerosol size distributions for the main k-Means cluster category: Traffic,
2 Nucleation and Urban Background. Only the main cities BCN, MAD and BNE were
3 considered.





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

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

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In order to analyse this, we link our discussion to that reported in Dall'Osto et al. (2013). At least two main different types of new particle formation events can be seen in the Mediterranean urban environment:

- (1) A regional type event, originating in the whole study region and impacting almost simultaneously the city and the surrounding urban background area;
- (2) An urban type event, which originates only within the city centre but whose growth continues while transported away from the city to the regional background.

The main difference between these two types resides in the origin of the nucleation events (regional scale in type 1 and urban origin in type 2). Moreover, the regional events are found to start earlier in the morning than the urban type and usually display the typical banana shape implying that photochemically nucleated particles experience subsequent growth. On the other hand, the urban type nucleated particles experience less growth, reaching sizes of 30-40 nm. The city of Brisbane exhibits new particle formation events starting in the morning (see Figure 5c), similar to the regional nucleation event types discussed in Dall'Osto et al. (2013). This may be due to the fact that the Brisbane site was located in a relatively clean environment. By contrast we find that the majority of new particle formation events detected in the other cities occur under the highest solar irradiance and thus around noon. Such events are characterised by a burst of particles lasting for about 3-4 h. A typical example is seen in Fig 5a. In the case of Madrid, there is no clear separation between the

morning rush hour traffic-related particles (20-100nm in size) and the nucleation particle burst at noon (20-40 nm), (Fig. 5b). This might be due to the similar PN concentrations exhibited by MAD_T1, MAD_T2 and MAD_NU clusters (see Fig.2c). The average diurnal PN considering Barcelona, Madrid and Brisbane size distributions (Fig. 6) shows that the typical nucleation event detected in urban environments consists of a particle burst that grows up to 20-40 nm in size. It occurs under high solar irradiance and temperature, and low relative humidity and NO_x levels. It also coincides with the development of the boundary layer and the dilution of road traffic emitted pollutants.