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Influence of seasonal factors on the atmospheric particle number concentration and size distribution in Madrid

F.J. Gómez-Moreno*, M. Pujadas, J. Plaza [2], J.J. Rodríguez-Maroto, P. Martínez-Lozano [1], B. Artíñano

CIEMAT, Environment Department, Av. Complutense 22, E-28040 Madrid, Spain

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ABSTRACT

The ambient particle number concentration and size distribution have been measured in an urban background site in Madrid, a continental Mediterranean area, over more than two years (Oct 2006–Dec 2008). The objective was to study the sources and processes affecting or contributing to fine and ultrafine particles in this area. They have been measured with a TSI–SMPS (15–600 nm) instrument and with a modified Vienna type DMA (3–80 nm) and a CPC 3025 (TSI) during 6 months. The average particle number concentration was lower than in other sites as it is an urban background site and because of its location in the Mediterranean area. The particle number concentrations have shown a clear seasonal influence: maximum values were observed every year in the period November–January, coinciding with atmospheric stagnant conditions and pollution episodes, while minimum values were measured in springtime, a period in which wind speed produced high atmospheric dilution. The Aitken and accumulation modes have shown similar seasonal behavior, with two maxima related to vehicle emissions. The nucleation mode had a third maximum observed at noon during spring and summer. The size distributions were bimodal during most of the time: the first mode was centered on 20–50 nm and was associated with fresh particles related to vehicle exhaust emission; the second mode, between 50 and 160 nm, mainly corresponded to the evolution of the first mode. The evolution of the size distributions reveals a marked annual cycle related to the season, with an increase of median diameters during summer and a decrease during winter. Different evolutions of particle size distribution corresponding to different meteorological and seasonal scenarios were identified. The influence of higher wind speeds on particle size distribution has been confirmed to cause a decrease in the particle number concentration and in the size distribution mode. Particle nucleation is not a frequent phenomenon in this measurement site, where 63 events per year have been observed. They mainly occurred during spring and summer periods, with the minimum number during winter. This suggests that insolation and temperature are important variables in nucleation. Class Ia nucleation events mainly occurred during spring and summer. High wind speeds were important during class II events, as the particles suffered low growth or lost their semivolatile compounds.

1. Introduction

Atmospheric particles can affect air quality and human health in urban areas (Dockery and Pope, 1994). The health effects of particles are linked to particle size, as this parameter determines the region of the respiratory system in which the particle will be deposited. Some toxicological studies have even indicated that toxicity per unit mass increases as particle size decreases (Lingard et al., 2005; Oberdorster, 2000). At the same time, atmospheric aerosol particles can play an important role in global climate through the Earth's radiation budget (IPCC, 2007). The quantification of aerosol radiative forcing is more complex than the quantification of greenhouse gas effects because aerosol mass and particle number concentrations are highly variable in space and time (heterogeneity). A detailed knowledge of some chemical and physical properties of aerosols is needed to estimate and predict direct and indirect forcing. Several parameters such as size distribution changes could become relevant to perform these estimations; it is therefore important to characterize the particle size distributions in different geographical areas. For this reason, in the last decade measurements of particle number concentrations and size distributions have been performed on a long-term basis in different locations in the world.

* Corresponding author. Tel.: +34 91 4962543; fax: +34 91 3466212.
E-mail address: FJ.Gomez@ciemat.es (F.J. Gómez-Moreno).
[1] Present address: ITB–CNR, Segrate, Milan, Italy.
[2] In memoriam.

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The Mediterranean area has some characteristics that make it different from other European scenarios. Climate is warmer than in other European areas due in the case of the Iberian Peninsula to the constant influence of the semi-permanent Azores high-pressure system and as a result precipitation amounts are low, especially in summer. It has an abrupt topography with coastal ranges influencing the synoptic winds, and there are intense temperature, humidity and rainfall contrasts between seasons (Querol et al., 2009; Millán et al., 1997) among other characteristics. Although most of the territory is covered by typical Mediterranean species (coniferous, oaks trees and shrubs), this area includes extensive regions of semi-arid soils and large quantities of biomass are not available as fuel for domestic heating systems as they are in central and northern Europe. This last fact produces different emissions profiles in these areas. Throughout the year, but especially during summer, there are events of African dust outbreaks with a strong influence on the aerosol load. The insolation is very high, producing an important rate of photochemical reactions, i.e. organic compound oxidations whose heavier mass allows them to be incorporated into the existing particles that grow, increasing their size. This also influences the potential new particle formation when none or very few particles are available.

Van Dingenen et al. (2004) compiled data on physical characteristics of aerosols, including particle distributions measured at 15 sites throughout Europe, and compared the different type of locations and periods of the day using long-term averages. This work showed that there is a lack of data of this kind in the Mediterranean area and in Eastern Europe. Petäjä et al. (2007) tried to fill this data gap by measuring in Marseille and Athens during an intensive campaign in both places in a summer month; Pey et al. (2008) did the same in Barcelona during one year and Costabile et al. (2010) did so in the area of Rome during one year and a half. Also significant is Rodríguez et al. (2007), where two Mediterranean sites (Barcelona and Ispra (IT)) are compared with London. Putaud et al. (2010) have recently updated the Van Dingenen et al. (2004) review and incorporated further data on measurements of the particle number concentration. It also includes new data from some campaigns in Portugal (Sangres and Mt. Foia) and in Milan. Fernández-Camacho et al. (2010) discussed one year and a half of measurements in Huelva, in southwestern Spain. A larger database in this geographical area will help to understand atmospheric aerosol behavior under Mediterranean continental conditions.

Meteorology and seasonality affect both particle size distributions and concentration in two different ways. On the one hand, they affect the boundary layer stability. This is, in the Iberian Peninsula the boundary layer is more stable during winter than during spring, so that particle concentrations are higher in the former season as the air volume for dilution is smaller. On the contrary, strong winds can either produce lower concentrations (Kumar et al., 2008a,b) or higher ones by re-suspension processes for particles larger than 100 nm (Charron and Harrison, 2003). The influence of these strong winds on the particle size distribution has been studied in a few works. Agus et al. (2007) observed a shift in the size distribution to smaller diameter particles at the same time as the Aitken mode region was reduced on windy days. Hussein et al. (2006) found a good correlation between particle number concentration and ambient temperature and local wind conditions in Helsinki.

In addition, meteorology and seasonality also affect the particle emission profile, e.g. heating system emissions during winter, and the generation of new particles, e.g. particle nucleation during spring and summer. But, in the Madrid area, not only emitted or generated particles coexist as it is also possible to find particles transported from other sites. The most typical long-range transport processes of aerosol in this region are the African dust outbreaks (Salvador et al., 2008), which will not significantly influence on the submicron particle concentrations and distributions (Pey et al., 2008), probably because they may act as condensation sink for those gases which can nucleate.

The seasonal effects on the particle number concentration have shown annual cycles of different particle size. Laakso et al. (2003) found in several Finnish sites a maximum in the nucleation mode particle concentration in spring and a second maximum in the Aitken mode in autumn.

The current work is aimed at studying the sources and processes affecting or contributing to fine and ultrafine particles in a representative continental Mediterranean area for the period October 2006–December 2008. To reach this objective, the work focuses on the seasonal evolution of the particle number concentration and distribution, and particularly the wind speed effects on both parameters. Additionally some nucleation events have been identified and characterized to find out the most likely conditions to lead to their appearance in the measuring site. This study has been performed at CIEMAT, an urban background site in Madrid, in the central part of the Iberian Peninsula.

2. Experimental

2.1. Description of the measurement site

The Madrid metropolitan area is located in the center of the Iberian Peninsula, bordered by the Sierra de Guadarrama (a high mountain range, 2400 m) 40 km from the city to the north–northwest, and by lower mountainous terrain to the northeast and east. The metropolitan area of Madrid has more than 6 million inhabitants and more than 2.5 million residents live in the surrounding towns. It comprises a car fleet of 4 million vehicles (fifty percent of which are diesel powered, including more than six hundred thousand medium- and heavy-duty trucks) with very intense traffic on weekdays on the connecting roads and the two existing ring roads. In addition to the regional fleet, there is an important number of trucks crossing the region, as Madrid is a relevant crossroads and includes a large dry port. Since its industrial activity consists essentially of light factories, the Madrid plume is typically urban, fed by traffic emissions and also by heating systems in winter. These features, together with the long distance between the Madrid metropolitan area and other significant urban or industrial areas in Spain (around 200 km), allow studying its plume as a typical urban plume.

The weather in Madrid is typical of a mid-latitude continental area, with hot dry summers and cold winters, most days being under clear-sky conditions. Mean annual precipitation is around 400 mm, mainly concentrated in the autumn and spring months. Previous studies focused on air pollution episodes in the Madrid air basin have characterized their driving meteorological conditions, as well as their typical atmospheric transport patterns (Plaza et al., 1997; Pujadas et al., 2000; Artíñano et al., 2003). In summer, the development of strong thermal convective activity and the influence of the mountains produce characteristic circulations and mixing layer development (Crespí et al., 1995). In winter, the general synoptic situation leading to the occurrence of episodic events corresponds to stagnant anticyclone conditions, light winds and clear-sky conditions, with the usual formation of radiative nocturnal surface inversions. That is why the worst pollution episodic situations in this region usually coincide with typical winter weather.

The measurements analyzed in this work were carried out at the CIEMAT facilities (40° 27.5′N, 3° 43.5′W), located in the NW corner of the city of Madrid, which can be considered as an urban background site (Fig. 1). It is close to a park, Dehesa de la Villa (71 ha),

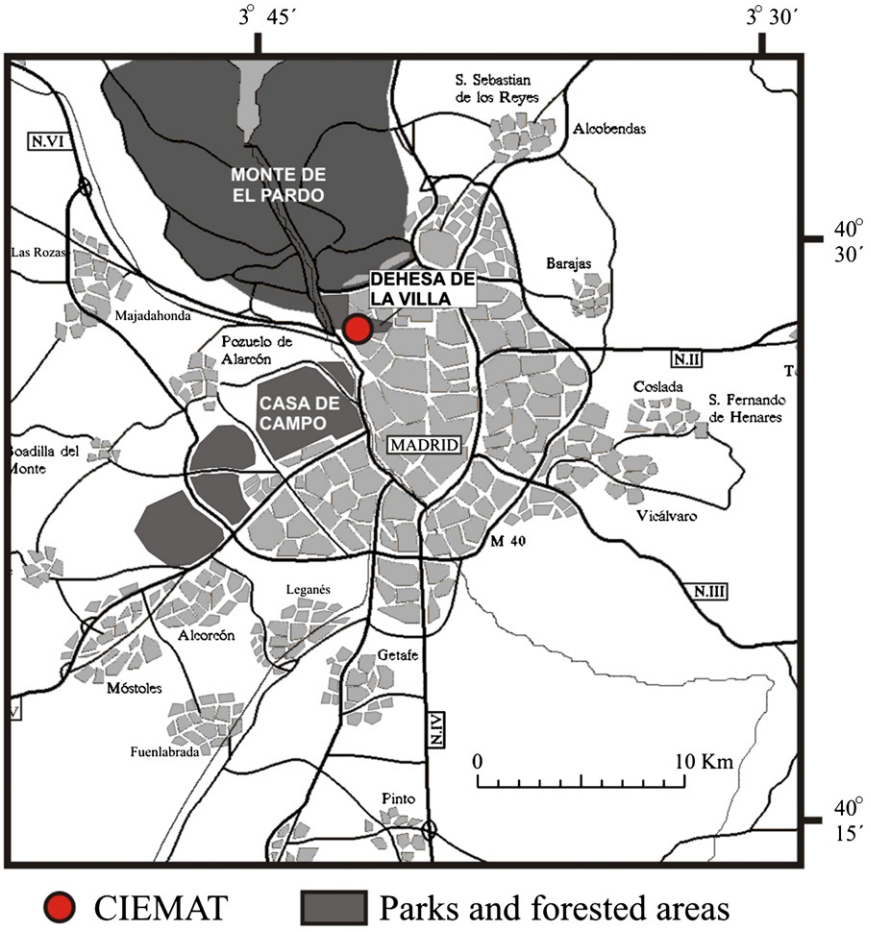

Fig. 1. Location of the measurement point (CIEMAT) in the Madrid area. It includes the biggest parks which could affect some measurements.

and not very far from Casa de Campo (1723 ha), a bigger park in the metropolitan area. An important forested area, Monte del Pardo (16 000 ha), extends over the north of the city. This particular location of the experimental site in the city border allows receiving different kinds of air masses depending on the wind direction. This implies the arrival of air masses with different origins, characteristics and pollution levels.

2.2. Instrumentation

The particle size distributions were measured by a TSI–SMPS (DMA 3071 and CPC 3022) (Stanier et al., 2004; Wang and Flagan, 1990) for the range 15–600 nm and by a home-built modified Vienna type DMA and a TSI–CPC 3025 for the range 3–80 nm. The latter DMA ($R2 = 33$ mm; $R1 = 25$ mm; $L = 90$ mm) features an exhaust path with reduced pressure drop, thereby allowing high flow rates to be reached (i.e. Reynolds numbers) with modest pumping capacity. The soundness of this prototype in the nanometer range was tested during a series of preliminary experiments measuring electrosprayed tetraheptylammonium ions (Rosell et al., 1996). For the flow rates used during these measurements, the resolution was similar to the traditional Vienna type DMA. The system, namely the DMA voltage ramp and CNC signal collection, was controlled through a LabVIEW home-developed code. The SMPS worked in scanning mode and was available for the period October 2006–December 2008. The modified Vienna type DMA worked in step mode and was available from March to October 2007. Both cases had the exception of periods in which the instruments were checked, revised and occasionally repaired.

A weatherproof inlet was used to prevent rain entering the sampling line. This aerosol sampling point was around 2-m high and the line was 2-m long before the sample was neutralized by a radioactive source (Kr-85). After this neutralizer, the flow was split into two secondary flows before reaching the DMAs. Both systems were located in a laboratory continuously ventilated with outside air for radiological reasons, so that the relative humidity inside and outside were similar. As the sheath flow rate used by both DMAs was taken from indoor air in an open loop, the particle size distribution was measured close to ambient conditions (Agus et al., 2007; Mäkelä et al., 2000). In the SMPS instrument each measurement cycle required 12 min, while in the modified Vienna type DMA it required 20 min.

In addition to particle size distributions, several meteorological parameters were measured at the experimental site by a permanent tower: wind direction and speed, precipitation, solar irradiance, temperature, humidity and pressure. Furthermore, some gaseous and particulate measurements were continuously and routinely performed at the site. These measurements have been used to support the result discussion.

3. Results

3.1. Particle number concentrations

The particle number concentration obtained by the TSI–SMPS (15–600 nm) varied along the measurement period in a seasonal basis. The average total concentration was smaller during 2008 (7325 cm^{-3}) than during 2007 (9918 cm^{-3}), which is related to the

higher average wind speed (3.5 m s^{-1}) that year than during 2007 (3.1 m s^{-1}) and the occurrence of several windy periods during the spring months in 2008 (Fig. 2). Instead, during the winter of 2007 there were several strong inversion periods associated with very light or calm winds. In Putaud et al. (2010) it is possible to find a summary of several measurements done in Europe. In their annex 3 and Fig. 4 it is clear that the lowest concentrations were measured in southern Europe compared with central and northwestern Europe. This is caused by the differences in temperature, boundary layer behavior and sun hours, among other ambient conditions, between northern Europe and the Mediterranean area, as has been previously mentioned. The concentrations obtained in Madrid had similar values to those for Ispra (near city site), and somewhat lower than in a Barcelona urban site. In the case of the Sagres and Mt Foia rural sites, their concentrations were lower in summer. There is also a clear decrease in the particle number concentration when moving from urban to rural stations (Putaud et al., 2010). As the CIEMAT site is an urban background site, the concentration measured is between that of a southern city and a rural site, similar to a near city site. In the Iberian Peninsula, Fernández-Camacho et al. (2010) measured a particle number concentration of 22,000 cm^{-3} in Huelva, a higher value probably because the site is affected by vehicle and industrial emissions.

Following the work of Hussein et al. (2004), the particle number concentrations have been integrated from the number size distributions for different intervals: the total range, the nucleation mode (dp $<$ 30 nm), the Aitken mode (within 20–100 nm) and the accumulation mode (dp $>$ 90 nm). The averaged values for every month with more than 50% of available data are shown in Fig. 3. It can be seen that in every year the maximum concentration was reached in November–January, a period prone to strong thermal inversion formation. The highest concentrations were reached in January 2007, coinciding with maximum values reached by other different pollutants routinely measured at the site, i.e. elemental carbon, particulate nitrate, nitrogen oxides. The minimum particle number concentration values were reached in springtime, when the high wind speeds produced the highest particle dilutions. The lowest concentrations were measured during the period March–May 2008, exactly when the wind speeds were the highest (a mean value of 4.2 m s^{-1} for March) in the experimental period, and the rains were also greater than in 2007. For the entire period the Aitken mode was the main mode, while the nucleation and accumulation modes had similar concentrations, or possibly slightly higher concentrations for the former.

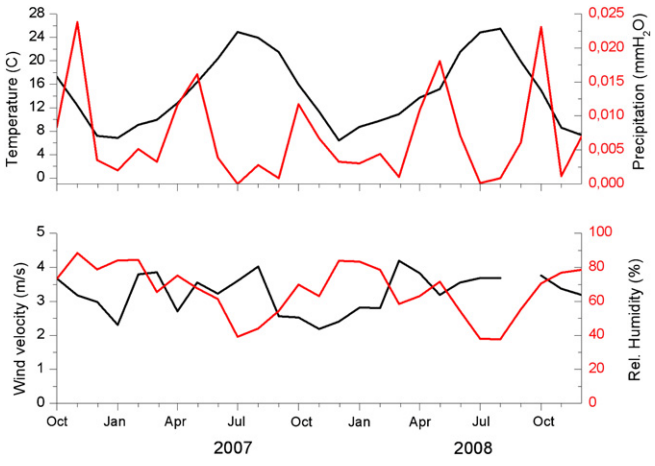

Fig. 2. The monthly averaged evolution of the main meteorological parameters measured at the measurement site.

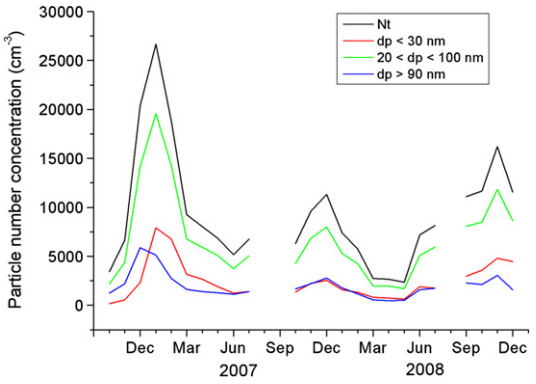

Fig. 3. Evolution of the particle number concentration during the measurement period. The total and the different mode concentrations are shown.

The annual averaged daily pattern did not show big differences between the years 2007 (Fig. 4) and 2008. The daily evolution was similar for both years, with a maximum at 8 UTC corresponding to the morning traffic rush hour, and a second and smaller peak at 21 UTC associated with the evening traffic peak. Particles corresponding to this second maximum arrived at the sampling site some time after being emitted because of the transport delay, longer than in the morning. Because of the atmospheric dynamics associated with this area, the sampling point is downwind of the city during the morning, but not during the evening, so that the polluted air masses take a longer time to arrive (Pujadas et al., 2000; Artíñano et al., 1994). For this reason, their aging degree is higher when they arrive at the measurement site and the Aitken mode is more significant than in the morning. The decreasing sense for the mode concentrations was the same for both years: Aitken (7257 cm^{-3} on average for 2007 and 5336 cm^{-3} for 2008), nucleation (2848 cm^{-3} on average for 2007 and 2019 cm^{-3} for 2008) and accumulation modes (1930 cm^{-3} on average for 2007 and 1449 cm^{-3} for 2008). These peaks corresponding with vehicle exhaust emissions can be found in other cities, although the time can be somewhat different as a function of local habits and site location. Laakso et al. (2003) showed that in the Helsinki urban area the maximum also corresponded with vehicle exhaust emissions in the early morning, but in other Finnish background stations it appeared between 15 and 18 h because of new particle formation. The decreasing sense for the mode concentrations was different in Helsinki (Hussein et al., 2004), where the order was nucleation, Aitken and accumulation modes, while in Barcelona (Pey et al., 2008) the order was the same as in Madrid. In Huelva (Fernández-Camacho et al., 2010), the daily evolution of the particle number concentration clearly showed

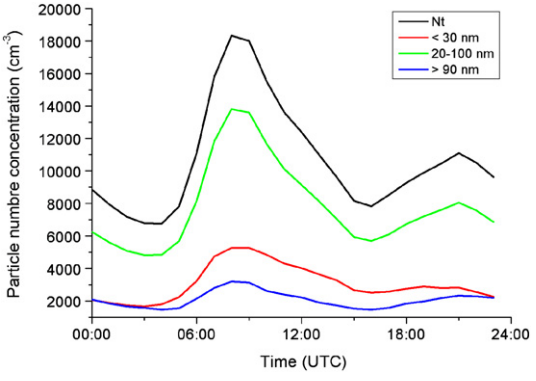

Fig. 4. The annual averaged daily pattern for the particle number concentration during the year 2007. The total and the different mode concentrations are shown.

a peak corresponding with vehicle exhaust emissions and a second peak around noon. This last peak was not related with traffic, so these particles can be from industrial emissions or from new particle nucleation. The fact that it appeared also during the weekend pointed toward the second possibility.

The seasonal variations of the averaged daily patterns of the total particle number concentrations were studied for spring (April, May, June), summer (July, August, September), autumn (October, November, December), and winter (January, February, March). The two previously described maxima remained (Fig. 5) throughout the four seasons, although the morning maxima appeared at two different positions depending on the local standard time (winter UTC+1, summer UTC+2). The evening peak was recorded at the same time in both years but it was better observed in winter than in summer, in spite that the weather did not allow this pattern to be produced during winter 2008. A possible third maximum could be observed around noon during the 2007 and 2008 spring and summer seasons, which could correspond to some nucleation episodes, as will be shown later.

Daily patterns were very similar for spring and summer of 2007. In autumn there was an increase in the morning maximum, which became much more important in winter when the maximum reached double that of the autumn one. The main reason for this high value in winter was the occurrence of several aforementioned long stagnant periods, mainly in January. During the year 2008 a different seasonal behavior was observed. Summer and spring had a similar pattern, but the total particle concentration was higher during summer. Autumn and winter also had similar patterns, but in this case the concentration was lower in winter, just the opposite of the previous year. The main reason for this opposite behavior is the different meteorology that did not allow the occurrence of long and frequent stagnant periods during 2007 autumn and 2008 winter as they occurred during 2007 winter and 2008 autumn.

The most interesting mode of the three analyzed was the nucleation mode, as it showed a slightly different behavior (Fig. 6). The autumn and winter patterns were similar to the total number concentration ones (Fig. 5) but during the spring and summer of 2007 and 2008 a third maximum was occasionally observed at noon. This was very clear during the 2008 summer (Fig. 6b), when this noon peak reached the same values as the emission peak during the morning and the two did not overlap. The 2007 summer showed a similar behavior. These peaks corresponded to nucleation episodes, as was confirmed subsequently by the particle distribution evolution. In the Mediterranean area, Pey et al. (2008) also observed different seasonal behavior for the nucleation mode compared with the Aitken mode. There was a secondary maximum observed at midday during summer, not observed during winter and not correlated with the traffic markers, which can be attributed to photochemical nucleation. Hussein et al. (2004) showed the daily patterns of the number concentration for the different seasons in the Helsinki area. They observed a clear variation in the concentration for the nucleation mode with two peaks related with vehicle exhaust during winter and spring and one during summer and autumn. A third peak around midday was not observed as it has been in the southern Europe.

3.2. Particle number distributions

It has become traditional to describe the particle size distribution by means of the sum of several lognormal distributions (Van Dingenen et al., 2005; Hussein et al., 2004). Each mode can be

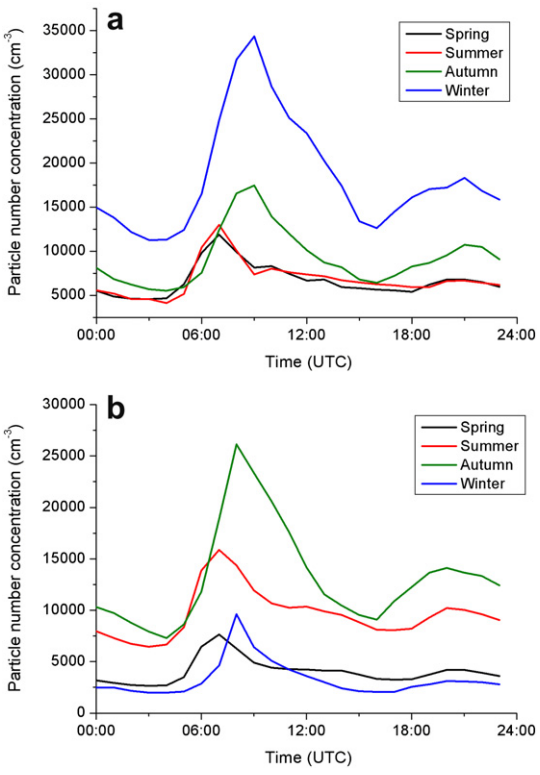

Fig. 5. The seasonal averaged daily pattern for the total particle number concentration during the years: (a) 2007 and (b) 2008.

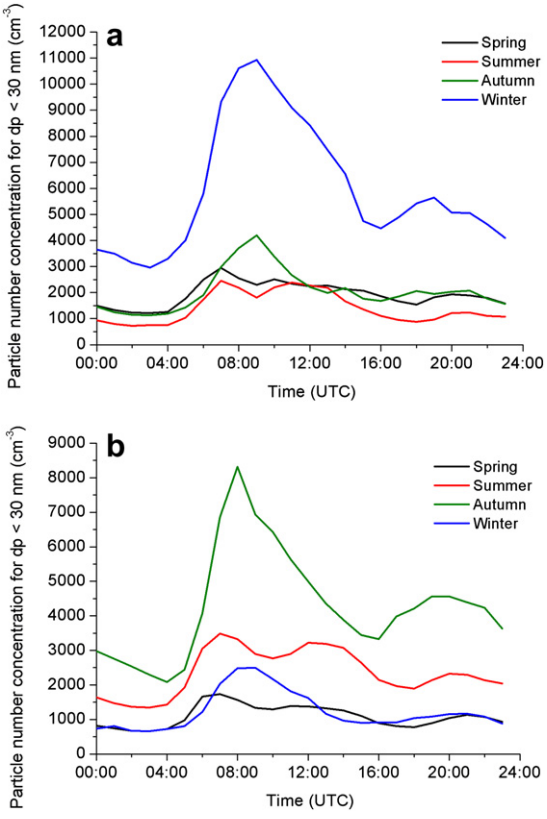

Fig. 6. The seasonal averaged daily pattern for the particle number concentration for dp <30 nm during the years: (a) 2007 and (b) 2008.

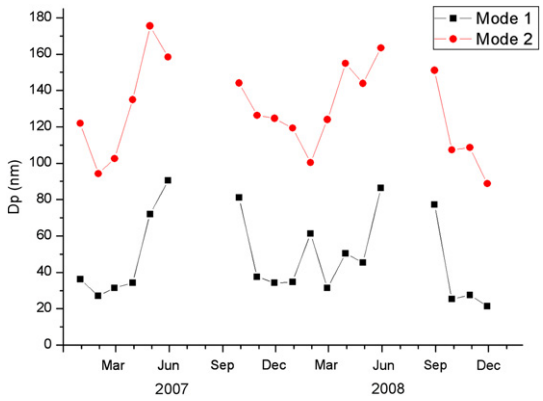

Fig. 7. Median diameters evolution during the years 2007 and 2008.

defined by three parameters: the median diameter, the geometrical standard deviation and the particle concentration. Mäkelä et al. (2000) evaluated the number of modes that were able to describe the particle size distributions. They found three typical modes, those already mentioned in the previous sections. But occasionally, a fourth and a fifth mode can also arise (Agus et al., 2007). The fitting procedure must therefore take into account the scientific experience and the previous information obtained in the sampling site. In this sense, Mäkelä et al. (2000) assumed the existence of two modes: the Aitken and accumulation modes, and the nucleation mode in some occasions, depending on the particle number noise and concentration ratio. In the current study, the situation was similar and the nucleation mode was mostly observed during some periods of the spring and summer, in periods when the other two modes presented very low concentrations.

The particle size distributions obtained during both years (2007 and 2008) were monthly averaged and later fitted to a bimodal lognormal function. The first mode corresponded to the vehicle exhaust emission particles and was usually centered on 40 nm. This mode value is somewhat higher than those measured in sites closed to a road (Buonanno et al., 2009; Hussein et al., 2007), which could be due to a certain aging of these particles during transport to the measurement site. The second mode corresponded mainly to the aged particles mode and the median sizes were between 80 and 180 nm, although a small fraction could be due to vehicle exhaust emissions in this size range. The evolution of the median diameters can be found in Fig. 7. It is interesting to note that both years exhibited a similar seasonal trend, with an increase in both median sizes during summer and a decrease during winter. This behavior has been associated with the atmospheric mixing layer characteristics of this area (Crespí et al., 1995) and the photochemistry of the precursors. During summer periods this layer is larger and the aerosol can remain suspended and recirculating for several days. As the gaseous compounds that can condense onto the particles are more diluted in summer than in winter, the particle growth rate is lower in summer but their longer atmospheric lifetime enables them to reach coarser sizes, as the associated photochemistry is more intense and takes longer periods of time. During winter the

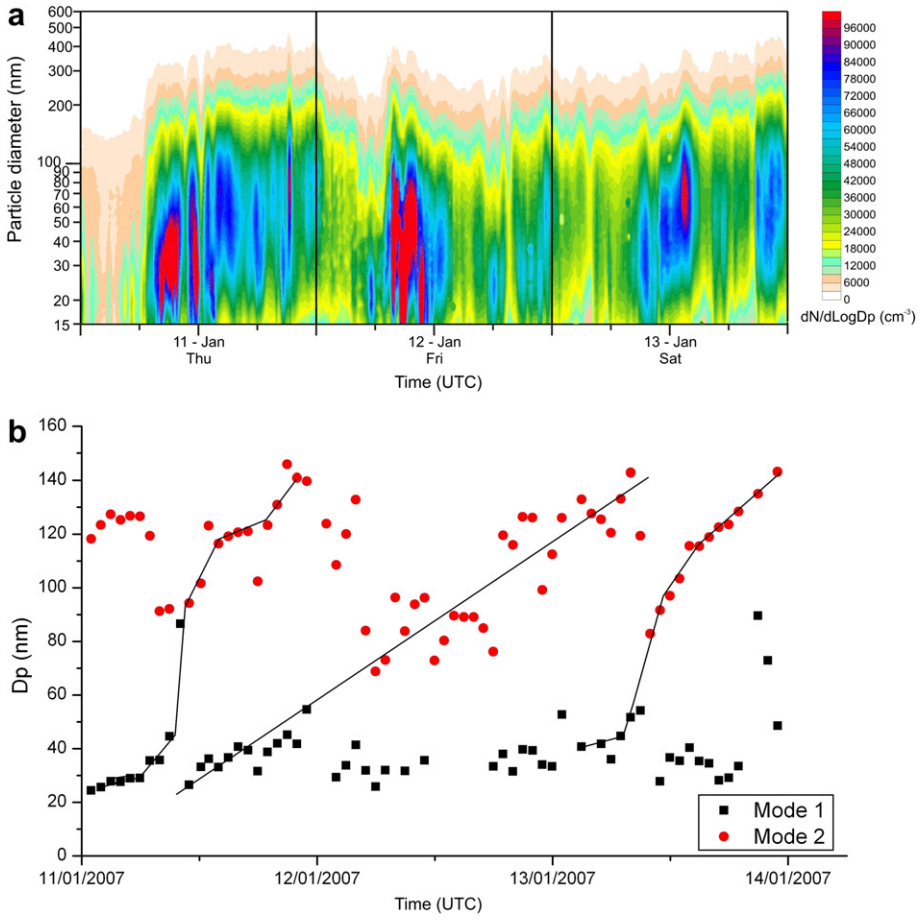

Fig. 8. Evolution of a) particle size distribution, b) median diameters for the wintertime period 11–13 January 2007, it includes the tendency lines.

particle and gaseous compounds concentrations are higher and the boundary layer is narrower, enhancing particle growth but during shorter periods. This behavior in winter has been observed in other locations and even with greater intensity. In Milan (Rodríguez et al., 2007), the lower temperatures and boundary layer depth increased the condensation material concentration, enhancing condensation. As a result the particle growth rates were higher than in Madrid and reached coarser sizes in winter than in summer. In London (Rodríguez et al., 2007), the concentration of gaseous precursors is not so high, and in summer with active photochemistry the particle growth allows reaching bigger sizes than in winter, a similar behavior to Madrid. In Barcelona (Pey et al., 2008) the median diameters do not show a clear tendency along the year. The site location is also important in the evolution of the median diameters. Hussein et al. (2004) measured in two different locations in Helsinki, both of them considered urban sites. In the first case, Siltavuori, the maximum median diameters were observed during summer and the beginning of autumn for the period 1998–2000. In the second site, Kumpula, the maximum median diameters were found during autumn and the beginning of winter for the period 2001–2002. To understand the annual evolution of median diameters it is necessary to take into account the individual characteristics of the measurement site, its associated photochemistry and the boundary layer behavior in the area.

This behavior in Madrid can be better observed in several particular cases. An example of particle growths during winter is shown in Fig. 8a, corresponding to 11–13 January 2007. On both the 11th (Thursday) and the 13th (Saturday), the meteorological situation produced stagnation conditions allowing an evolution of the air masses without influence of advection. A maximum in the size number distribution appeared around 20–30 nm, corresponding to the morning traffic rush hour and later shifted to bigger sizes due to particle growth. These high vehicle exhaust emission periods were identified in the primary gaseous pollutant measurements. A second maximum was observed in some periods when there was a mix between primary and secondary gaseous pollutants because the air mass was already aged, so that this second maximum corresponded to secondary particles. Fig. 8b shows the evolution of the median diameters obtained by fitting the measured distribution to a bimodal distribution. During this period a maximum growth rate of 6.2 nm h^{-1} was reached.

Another example of the evolution of the size distribution is shown in Fig. 9a with the data from Monday 7 to Wednesday 9 July 2008. It can be seen how the main mode increases its size along the period until it reaches an asymptotic value. Fig. 9b shows how the second mode had a higher median diameter during this case than during winter conditions, as it evolved in the range 80–160 nm during summer and between 70 and 140 nm during winter. In the afternoon of the 7th, the first mode around 40 nm started to increase its median in a process which lasted until the end of the 9th when a median size of 150–160 nm was reached. This process was simultaneous with new particle emissions, which reduced the median size during a short period. The average growth rate during this period was 2.6 nm h^{-1}, smaller than during the winter. This kind of behavior was more typical during summer, when there is a larger mixing layer and a higher dilution, which means a smaller concentration and therefore a slower growth. Although the higher dilution volume produces a slower particle growth, the higher photochemical activity would determine the growth of the particle by the oxidation of some compounds (i.e. volatile organics), facilitating their addition to the particle. This higher activity and the longer periods of particle growth help to obtain bigger particle

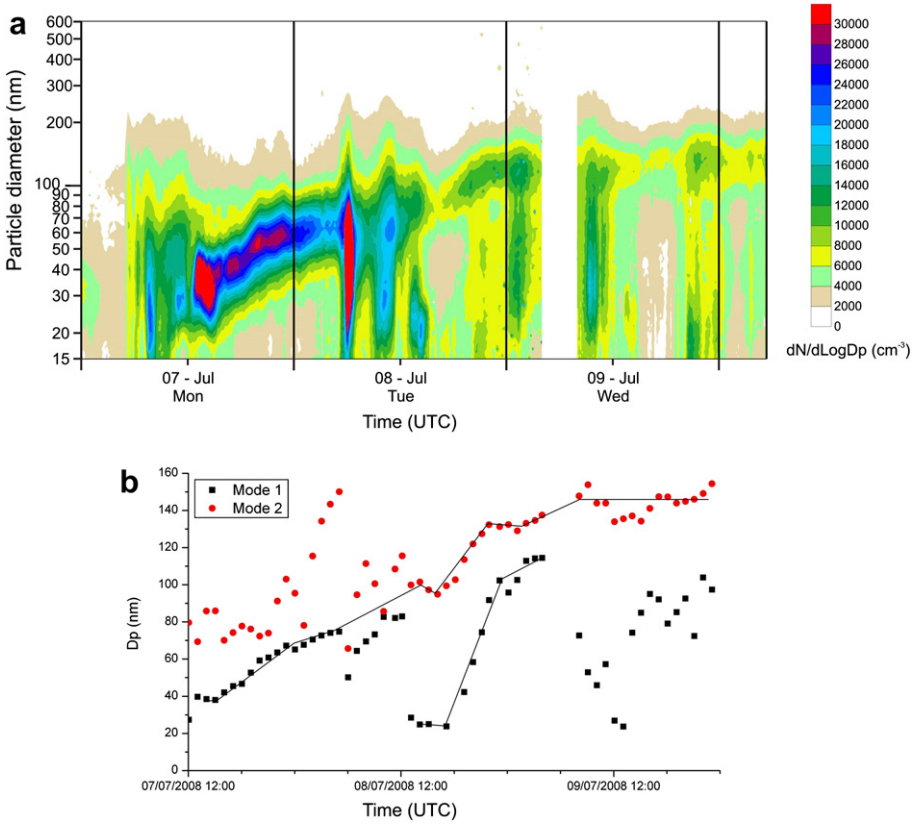

Fig. 9. Evolution of a) particle size distribution, b) median diameters for the summertime period 7–9 July 2008, it includes the tendency lines.

diameters during summer than during winter, as can be seen in the asymptotic diameter shown in the figures. In the winter example the growth period was limited to one day, but the summer meteorological conditions allowed the growth to be maintained for several days.

3.3. Wind speed influence

High wind speeds result in plume dilution and reduce the time for particle aging. Therefore, they influence not only the particle number concentrations but also the size distribution modes (Charron and Harrison, 2003; Agus et al., 2007). To study this influence, a simple statistical analysis was done by averaging the size distribution during selected periods with low wind speed, between 1.3 and 1.9 m s^{-1} (Fig. 10a), and high wind speed, between 4.5 and 7.3 m s^{-1} (Fig. 10b). In the first group, the modes corresponding to both fresh and aged particles presented comparable concentrations. In the second group, the aged particle mode concentration was much smaller than the fresh particle mode. Fig. 10 also shows that the increase in wind velocity caused a general decrease in the particle number concentration and a reduction in the particle size of the emission mode. The explanation of these effects is that the higher wind speeds favored the dilution of the emissions produced by the city with clean outer air masses. This lowered the total particle concentration and prevented the typical increase of the mode between 80 and 100 nm from smaller primary particles. This same behavior has been previously observed in Leicester (UK) (Agus et al., 2007). Decreases of 30% in the nucleation modal size and 70% in the Aitken modal size were observed in a roadside location when the wind speed increased from 0 to 4 m s^{-1}. Similar results were obtained in central London by Charron and Harrison (2003). The fact that the high wind speed maintained the size distribution with the maximum in a very small size means that these periods of time can be classified as class II nucleation events, as discussed in the next section.

To study the influence of wind speed on size distribution in detail, the period 4–11 February 2007 has been selected for analysis. During this period there were 3 days with a wind speed under 3 m s^{-1}, 2 transition days with an increasing wind speed up to 5 m s^{-1}, and 3 more days with a wind speed above 5 m s^{-1} (Fig. 11a). During these last three days, the wind direction remained approximately constant from the southwest, the experimental site being downwind of the residential areas. A clear decrease in particle number concentration was observed, Fig. 11b, as the wind speed increased and produced a dilution effect, such that on 5 February there was a mean number concentration of 3.2×10^4 cm^{-3} and on 11 February it was 3.9×10^3 cm^{-3}, an order of magnitude smaller. Concerning the mode displacement, during the stagnation period (low wind speed), the first mode was around 30 nm and after a period of time it was possible to surmise a second mode around 80 nm, caused by particle aging. During the vented period the first mode was shifted to smaller sizes than under non-vented conditions, even smaller than 15 nm, and only a branch of the distribution is seen. A possible reason for this behavior is that the dilution effect produced by high wind speeds reduces the organic concentrations in the gas phase and produces a higher volatilization of the organic compounds from the particulate phase, thereby reducing particle size. This explanation is in agreement with Robinson et al. (2007), who established that the dilution effect on diesel particles was more intense than previously considered and

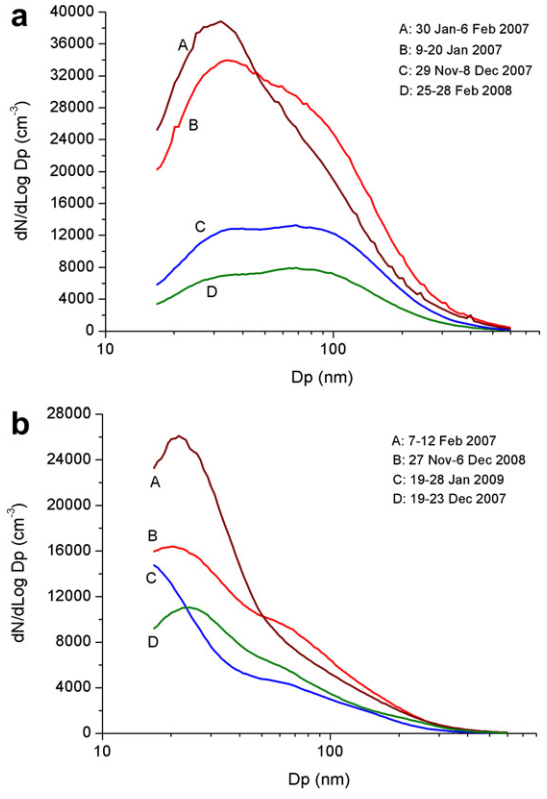

Fig. 10. Mean particle size distributions measured during low wind speeds (a) and high wind speeds (b). The wind speeds (m s^{-1}) in the (a) case are: A: 1.9, B: 1.3, C: 1.3, D: 1.6. In the (b) case, they are: A: 5.5 (from the third quadrant), B: 4.5 (from the first quadrant), C: 7.3 (from the third and forth quadrants) and D: 4.7 (from the third and forth quadrants).

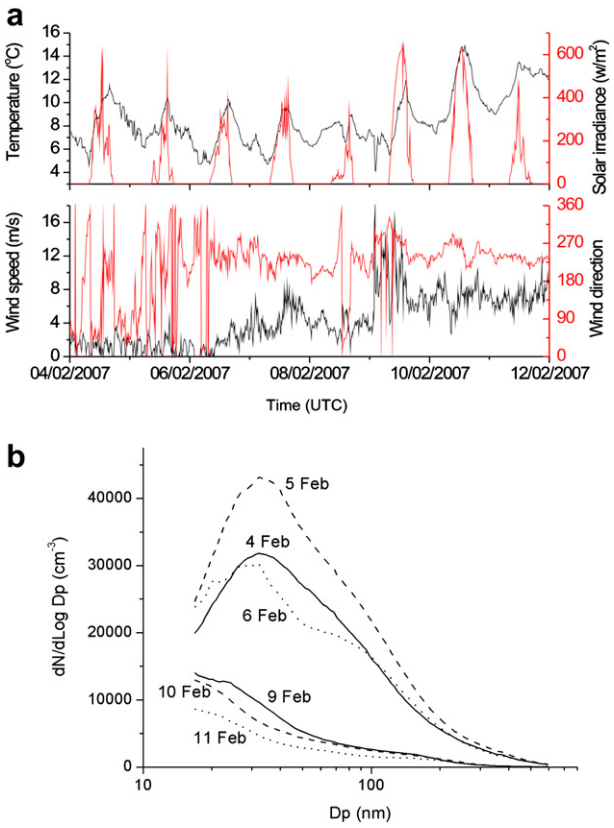

Fig. 11. Evolution of a) the meteorological parameters and b) daily averaged size distributions for the period 4–11 February 2007.

that an important mass fraction of these particles is shifted to the gas phase as the dilution factor increases.

3.4. Nucleation events

Previous TSI–SMPS measurements performed in this site suggested the existence of nucleation events. The lower limit of this instrument is 15 nm, constraining the complete observation of this type of events. In these previous cases, some situations with a clear and fast increase in particle concentration and size were detected, which allowed seeing the typical banana-shaped evolution, pointing toward nucleation cases followed by particle growth processes (Stanier et al., 2004). However, it was not possible to confirm this hypothesis because no instrument capable of measuring down to 3 nm was available during those periods. Again, in the period May–July 2007, there were similar distributions to those measured previously. Fig. 12a shows the period 10–15 July, an example of possible nucleation events, some of which have the typical banana shape. In some cases there were particles that could act as possible condensational sinks, albeit in low concentrations. After March 2007 and during six months, the nucleation events were confirmed by the use of a modified Vienna type DMA coupled with a CPC 3025, which allowed measuring particles under 15 nm and down to 3 nm. During most measurements the sizes at which the event started were close to 10 nm, but on some occasions the nucleation and growth of nanoparticles was observed from 3 nm at noon (see Fig. 12b (right) for 29 June 2007). These measurements confirmed the ones in which the modified Vienna type DMA was not available yet, although the uncertainty associated to the possible nucleation event determination and classification is higher in this case.

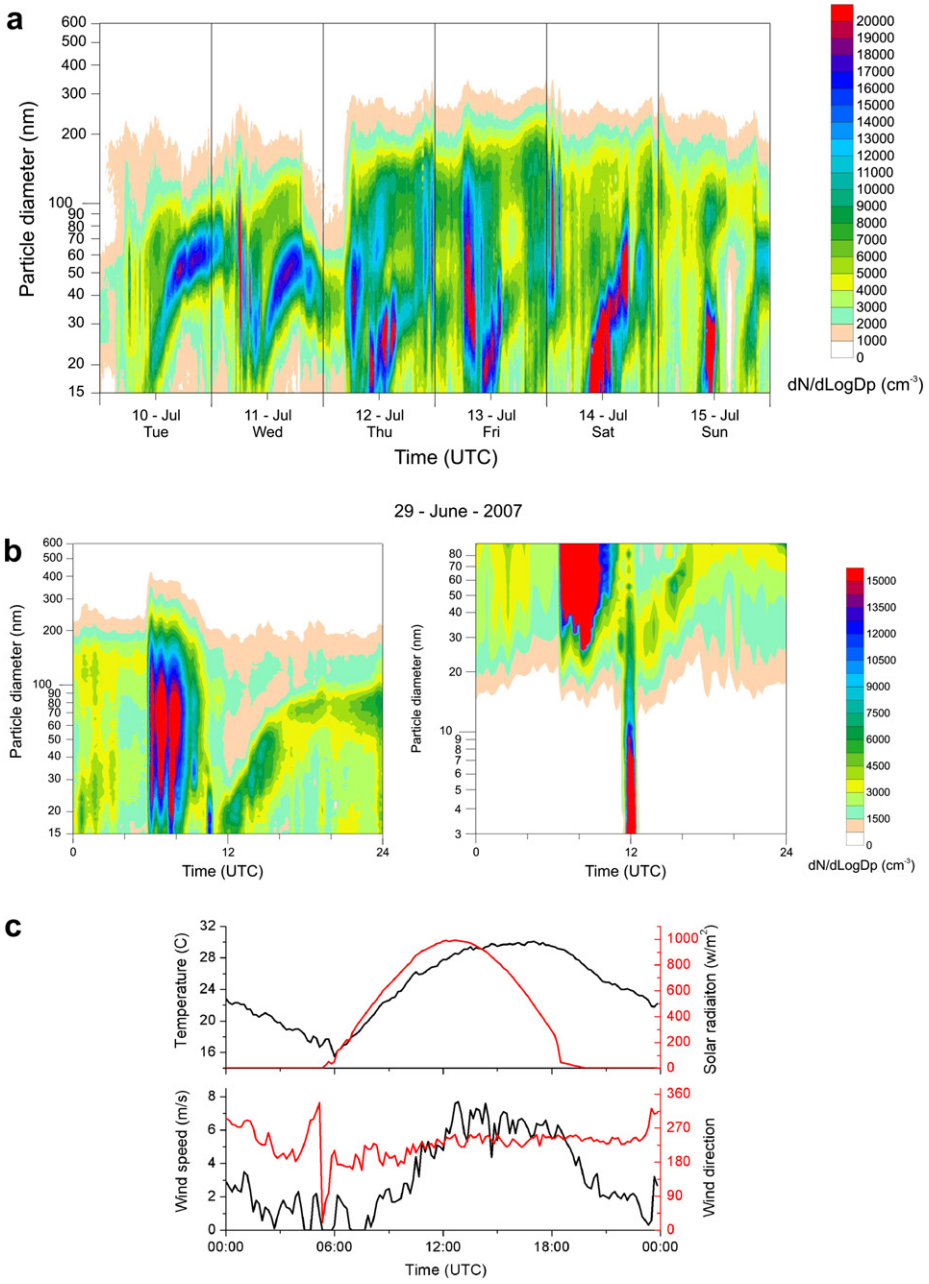

Fig. 12. Evolution of the particle size distribution (a) for the period 10–15 July 2007, when it is possible to see a possible nucleation event every day, (b) for 29 June 2007 measured by the SMPS (TSI) (left) and by a modified Vienna type DMA coupled with a CPC 3025 (TSI) (right). The meteorological parameters for 29 June 2007 are shown in (c).

64 nucleation events were recorded during 2007 and 63 during 2008. Thus, particle nucleation is not a frequent phenomenon in this area. Pey et al. (2008) observed in Barcelona 50 nucleation events over 399 days. In contrast, a higher number was found in at the San Pietro Capofiume station in the Po Valley area, a rural site in Italy (Hamed et al., 2007): 279 events over 769 days. In a northern location, a Finnish boreal forest ecosystem measurement station, Dal Maso et al. (2005) observed 699 events over 2892 days. These higher statistics in both sites are probably due to the rural background site characteristics. In Fig. 13 it is possible to find the monthly distribution of these events in Madrid. They mainly occurred during spring and summer periods, with the minimum number during winter. This behavior suggests that higher insolation and temperature are important factors in enhancing particle nucleation. Hamed et al. (2007) also report a maximum number of nucleation events during these months, and a minimum during winter at the San Pietro Capofiume station. Dal Maso et al. (2005) found a maximum during spring but not during summer, when a minimum appeared instead, probably due to changes in the air mass origin and composition during this period. This maximum during spring seems to appear in different locations (Stanier et al., 2004; Birmili et al., 2003).

Attending to the characteristics of each case it is possible to classify the nucleation events into three classes: Ia, Ib and II (Dal Maso et al., 2005; Cheung et al., 2010). Class I corresponds with events in which the particle growth rate can be determined or observed. In Class Ia the typical banana shape is clearly visible. In Class Ib some previous particles or the transport pattern can prevent seeing the banana shape, but the particle growth can be observed. Class II corresponds to a situation in which particle growth determination is not possible or the accuracy of the results is questionable. The classification of nucleation events is currently subjective and an overlapping of the classes may occur.

The observed nucleation events have been classified following the above criteria and can be found in Fig. 13. Class Ia events usually occurred during spring and summer, when there were biogenic emissions and high photochemical activity. They were mainly characterized by starting at noon, when the insolation is highest, there is a low wind speed and air masses come from sparsely populated areas. An exceptional case of this class of nucleation events in which it is possible to see the complete process is the one shown before in Fig. 12. Considering the wind directions (Fig. 12c), this variable indicated that the air masses were coming from the "Casa de Campo" park, where it is possible to find different types of trees: oaks, pines, poplars and chestnut trees among others. A possible hypothesis for explaining this particle growth is that it was produced by photo-oxidation of the biogenic organic compounds emitted by the vegetation from the "Casa de Campo" park (Pindado et al., 2009). In this case the gaseous pollutant measurements indicated the very low concentration of fresh anthropogenic emissions. This is an exceptional case because the wind speed was above 6 m s^{-1} and this allowed following the nucleation and growth process from 3 nm. For more common cases with low wind speeds, the nucleation process would start some kilometers away from the sampling point with the particles growing along the air mass trajectory, arriving at the site with diameters above 10 nm. In other cases, when the wind speed was very close to zero, the proximity of the "Dehesa de la Villa" park suggests another possible origin for the particle precursors.

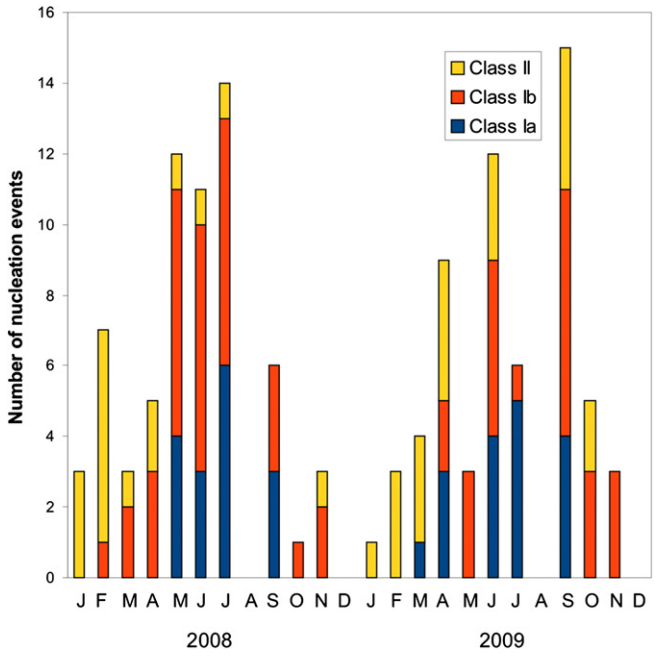

Fig. 13. Number of nucleation event classified and distributed by months along the measurement period. Data for August during both years 2008 and 2009 were not available.

Class II events mainly occurred during winter months, especially during 2007, and also during springtime. However, the influence of high wind speeds during these events was more important than that of the seasonality. In almost all the cases, the wind speed was above 4 m s^{-1}, reaching 8 m s^{-1} in almost half the cases. Under these wind speed conditions, the particles suffered low growth or could even have lost their semivolatile compounds, as discussed in the previous section. They usually started during the morning hours, so they were related with vehicle emissions and not with photochemical activity. Class Ib events had characteristics between those of classes Ia and II. They occurred during all the year, although in winter they had a low frequency. In almost all the cases the wind speed was below 4 m s^{-1} and the wind direction was similar to that of class Ia events or was rotating in the typical clockwise sense from northeast to west. This characteristic of transport to the measurement point and oscillations in the wind speed could be the reason why a complete banana shape growth was not observed. They usually started at noon, when the photochemical activity is high, and so they were related with particle nucleation and not with vehicle emissions. Hamed et al. (2007) also discussed the distribution of the classified events along the different seasons at San Pietro Capofiume station. They found that class II events were predominant throughout all the year and that class Ia events had a lower frequency, not appearing during October–January. Class Ia and Ib events had their maximum during the end of spring and summer.

4. Conclusions

This study presents the results obtained from the analysis of the evolution of the ambient particle number concentration and size distribution in Madrid in the period October 2006–December 2008. It is aimed at studying the sources and processes affecting or contributing to fine and ultrafine particles.

The average particle number concentration was low because this is an urban background site, similar to a near city site, and it is located in the Mediterranean area, where the concentration is usually lower than in northern and central Europe. The time series analysis has shown the seasons when extreme values are recorded in this area, and these have been associated with the prevailing meteorological conditions. It has been observed that the maximum particle number concentrations were reached during the periods November–January, when the boundary layer is small and pollution

episodes usually take place. The minimum values were measured during spring, when higher wind speeds produced a higher dilution and therefore an atmospheric cleanup. The Aitken and accumulation modes have shown similar seasonal behavior, with two maxima related to vehicle emissions. The nucleation mode had a third maximum observed at noon during spring and summer. This peak is typical for southern Europe.

The evolution of the size distributions reveals a marked annual cycle for two modes, that is repeated every year, also related to the season of the year and therefore to the prevailing atmospheric conditions. The monthly particle averaged size distributions shows a first mode corresponding to the emission one and centered around 40 nm and a second mode corresponding to the aged particles and centered between 80 and 180 nm. The two years presented the same seasonal trend with an increase of median diameters during the summer and a decrease during the winter, corresponding to the particle lifetime. In winter the growth period was limited to one day, but summer meteorological conditions allowed this to be maintained for longer periods. Not all the European sites have the same behavior. London and Helsinki had a similar annual cycle, but Ispra (IT) was different and Barcelona did not show a clear tendency. The individual characteristics of the measurement site are important for understanding the annual evolution of median diameters, as is its associated photochemistry and the behavior of the boundary layer in the area.

Particle number concentration and size distributions were affected by the dilution produced by high wind speeds. A general decrease in the number concentration has been observed when the wind speed is higher than a certain threshold around 3 m s^{-1}. Above this speed, the aged particle mode was reduced while the emission peak was shifted to smaller sizes.

Particle nucleation is not a frequent phenomenon in this measurement site, where 63 events per year have been observed. This is a higher number than in Barcelona but lower than in San Pietro Capofiume, a rural site in Italy, and in a Finnish boreal forest. In southern Europe they mainly occurred during spring and summer periods, with the minimum number during winter. This suggests that higher insolation and temperature are important factors in enhancing particle nucleation. Class Ia nucleation events usually occurred during spring and summer, when there were biogenic emissions and high photochemical activity. Class II events mainly occurred during winter and spring months, but the high wind speeds during these events was more important than the seasonality as the particles suffered low growth or they could even have lost their semivolatile compounds.

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