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Variations of urban aerosols in the western Mediterranean

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ABSTRACT

Real time measurements of number concentrations (13–800 nm, N_{13-800}) of size discriminated sub-micrometric aerosols and PM (0.3–10 μm) mass concentrations were carried out over a one-year-period at an urban site in Barcelona, North-eastern Spain. Annual mean levels of N_{13-800} were close to 17,000 cm^{-3}, and strongly dependent on road traffic emissions. Annual mean PM_{10}, $PM_{2.5}$ and PM_1 levels were 39, 25 and 18 $\mu g/m^3$, being highly influenced not only by road traffic but also by industrial emissions as well as natural events such as African dust outbreaks.

Variability of number concentrations and size distribution of sub-micrometric aerosols was strongly dependent on meteorology. Primary emissions exert a high influence on the variability of levels of ultrafine (<100 nm) particles under intense Atlantic advections (lowest PM levels), while coagulation and condensation processes are enhanced under urban pollution scenarios (highest levels of PM), and photochemical nucleation processes can be an important source of ultrafine particles at midday in summer (low PM levels). African dust episodes did not modify the total number but affected the $N > 400$ nm.

This study allows us to compare aerosol number and mass concentrations in air quality monitoring of an urban environment. Ultrafine particles measurements are indicated to detect the variability of primary traffic emissions, as well as some atmospheric processes. Measurements of PM levels are necessary to monitor other important PM sources in the studied area such as dust resuspension from road traffic or African dust.

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1. Introduction

Particulate matter (PM) pollution arises both from natural and anthropogenic sources. Many epidemiological studies show that atmospheric aerosols may produce adverse health effects, with recent studies revealing that coarser atmospheric particles are more related to respiratory diseases, whereas the finest particles seem to affect the cardio-vascular system (Pope et al., 2002, 2004; Wyzga, 2002; Dockery and Stone, 2007). The current legislation on Air Quality concentrates only on total mass of PM_{10} and $PM_{2.5}$ (the mass of the particles with an aerodynamic diameter below 10 or 2.5 μm, respectively), and relatively little attention has been paid to other parameters such as the chemical composition or the number concentration of sub-micrometric aerosols, SMA (13–800 nm).

Independently of the dominant natural origin of atmospheric aerosols on a global scale (IPCC, 2007), in urban areas the main source of atmospheric PM is road traffic (Morawska et al., 1998; Wehner et al., 2002; Zhu et al., 2002), with diesel vehicles in particular being associated with higher emissions of fine and ultrafine particles

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(Morawska et al., 1998; Harris and Maricq, 2001; Jacobson and Seinfeld, 2004; Rose et al., 2006), exceeding up to 10–100 times those from gasoline vehicles in terms of mass, and up to 10^5 times in terms of number concentration (Harris and Maricq, 2001). Previously published measurements (e.g. Morawska et al., 1998; Maricq et al., 1999; Harris and Maricq, 2001; Sakurai et al., 2003) have shown that gasoline and diesel vehicles both emit nanoparticles (<50 nm), mainly made up of sulphate and semi-volatile compounds such as organic species. In addition, diesel vehicles also emit accumulation mode particles (50–1000 nm), mainly composed of ten to thousands of spherules formed during the combustion process. With this in mind, in Spain over recent years there has been an increase in diesel vehicle use which, although initially associated with an attempt to reduce CO_2 emissions, is producing an increase in suspended particle levels, mainly in the <1 μm fraction (Pérez et al., 2008). This is causing concern for public health, as it becomes increasingly evident from toxicological studies that SMA could have a greater impact on health than coarser fractions with the same concentration and composition (Donaldson et al., 1998; Donaldson and MacNee, 2001). The problem is much less associated with the mass concentration of SMA than with particle number: in urban areas around 80% of the particles in terms of total number are under 0.1 μm (ultrafine particles) in size (Morawska et al., 1998; Wichmann et al., 2000; Rodríguez et al., 2007).

Once emitted, the evolution of atmospheric aerosols in the urban environment is affected by processes such as dilution, coagulation, condensation or deposition, which modify the number and/or the size distribution, and are influenced by meteorological parameters such as temperature, relatively humidity, wind speed, or amount of solar radiation. Furthermore, nucleation from previously emitted gases can strongly increase the particle number, displacing the size distribution to finer diameters. The effect of these processes affecting the number and size distribution of fine and ultrafine aerosols has been studied in detail in Northern and Central Europe (Nilsson and Kulmala, 1998; Wehner et al., 2002; Ketzel et al., 2004; Rose et al., 2006; Olivares et al., 2007), but these kinds of studies are scarce in southern Europe, especially in the Mediterranean area (Van Dingenen et al., 2004; Rodríguez et al., 2005). In the urban environment, during the tailpipe to road processes, the sharp drop in temperature generates high amounts of nucleation mode particles (Kerminen et al., 2007; Olivares et al., 2007). In addition, photochemical nucleation events can be frequent under specific conditions (Kulmala et al., 2004 and references therein; Minoura and Takekawa, 2005). On the other hand, coagulation and condensation increase the particle diameter, and coagulation also reduces the aerosol number (Zhang et al., 2004; Zhang and Wexler, 2004). The occurrence of these processes is highly dependent on the meteorology (Minoura and Takekawa, 2005; Kerminen et al., 2007) and also on the condensed species, the size of the aerosols and their chemical composition (Zhang and Wexler, 2002; Zhang et al., 2004; Zhang and Wexler, 2004).

Different studies on PM have been carried out at the same monitoring station or at other urban sites in Barcelona, focused on the interpretation of the variability of size segregated PM levels (Rodríguez et al., 2002; Viana et al., 2005) and on the chemical speciation of PM in different grains size (Viana et al., 2005; Pérez et al., 2008). Thus, the variability of PM levels and the interpretation of the chemical composition are well known for the study area, the results presented in this paper are the first measurements on the variability of number concentration and size distribution of fine and ultrafine aerosols in Barcelona. This is the first such study in Spain, with results on particle number being compared with simultaneous mass measurements obtained for different grain size fractions. Special attention is paid to the study of aerosol events such as photochemical nucleation, African dust or coagulation/condensation processes.

2. Methodology

From November 2003 to December 2004 measurements of particle number and size distribution of SMA were carried out at an urban background site with a high road traffic influence in Barcelona, North-eastern Spain (41° 23′ 05″ N; 02° 07′ 09″ E; 68 m.a.s.l.). This site is located on the roof terrace (two storeys, around 8 m above the ground) of the Institute of Earth Sciences "Jaume Almera" (Consejo Superior de Investigaciones Científicas: CSIC), in SW Barcelona, 150 m from the 9-lane Diagonal Avenue (traffic density 106.000 vehicles day^{-1}, Ajuntament de Barcelona), one of the busiest main roads in Barcelona.

The data collection system used comprises a Condensable Particle Counter (CPC) TSI 3022 connected to a Differential Mobility Analyzer (DMA) TSI 3071. This equipment provided a complete size distribution of the number of particles between 13 and 800 nm (N_{13-800}), with readings being recorded every 7 min by homemade software. Note that before particles enter the DMA, a volume of sampling air was dried with a system operated with silica gel, after which a zero filter was installed. When this air is mixed with the sampled air, the dilution system reduces the humidity of the ambient air, so that our measurements were carried out on dry aerosol particles (relatively humidity less than 20%). Before starting measurements the calibration of the CPC–DMA system was made at the ISPRA-JRC laboratories.

In the following sections we will refer to N_{xx-yy}, as the particle number in the size range xx–yy nm; DpN_{max}, as the diameter at which the number distribution of sub-micrometric aerosols reach their maximum concentrations; and dN/dlogDpN, as the number concentration normalized with respect to the diameter.

Simultaneously, levels of PM_{10}, $PM_{2.5}$ and PM_1 were obtained at the same site over the same collection period, using a laser spectrometer GRIMM 1108 which recorded PM levels on an hourly basis. The spectrometer data were corrected by comparison with simultaneous gravimetric measurements by using high volume samplers MCV-CAV (30 m^3/h) with DIGITEL PM1025 inlets (at least two PM_{10} and two $PM_{2.5}$ 24-h samples were collected every week, most of them in working days), in accordance with guidelines EC (2001).

Levels of gaseous pollutants were supplied by the Department of Environment of the Autonomous Government of Catalonia, and meteorological variables (atmospheric pressure, wind components, solar radiation, temperature and relative humidity) from a close meteorological station (100 m distant from our measurement site) located on the roof terrace of the Chemical and Physical Sciences Faculty of the Barcelona University (UB), have been used for interpretation.

Additionally, 120 h back-trajectories ending in Barcelona, different aerosol concentrations maps (BSC/DREAM, NAAPS, and SKIRON) and satellite imagery (SeaWiFS/NASA) have been daily analyzed to interpret different aerosol scenarios.

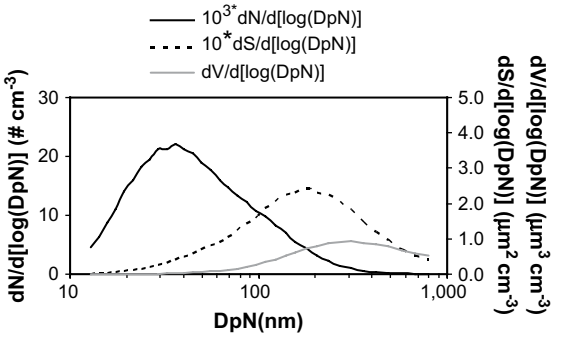

Fig. 1. Mean dN/dlogDpN, dS/dlogDpS, and dV/dlogDpV, obtained at Barcelona-CSIC for the period November 2003 to December 2004.

3. Results

During the study period the mean concentration of SMA was 17,000 cm^{-3}, which is similar to other European urban areas (Wichmann et al., 2000; Tuch et al., 2003; Van Dingenen et al., 2004; Lingard et al., 2006). The mean diameter of the SMA was 39 nm (Table 1 and Fig. 2), again being similar to results obtained in other urban background sites (Morawska et al., 1998; Stanier et al., 2004). Surface and volume maxima are obtained for the 168 and 324 nm fractions, respectively (Table 1 and Fig. 1).

Mean levels of PM_{10}, $PM_{2.5}$ and PM_1 in the same period were 39, 25 and 18 $\mu g/m^3$ respectively. These levels were within the range observed in other urban areas in Spain (Querol et al., 2004), but slightly higher if compared to other European cities (Van Dingenen et al., 2004). The currently operative European Air Quality Directive focuses on measurements of PM_{10} mass, fixing an annual average limit of 40 $\mu g/m^3$, and a maximum of 35 days per year when a daily limit value of 50 $\mu g/m^3$ PM_{10} can be exceeded. During our collection period we recorded 50 $\mu g/m^3$ exceedences on 81 occasions (making an average of 69/year), 15 being attributable to African dust influence. A new draft for air quality directive suggests an annual target of 25 $\mu g/m^3$ for $PM_{2.5}$. In this context our measurements demonstrate not only that the allowable number of annual exceedences of the PM_{10} daily limit value of 50 $\mu g/m^3$ is surpassed in our monitoring station, but also the average annual limits are in a critical situation.

3.1. Daily cycles and weekly evolution

Fig. 2 shows the mean weekly evolution of N, PM and gaseous pollutants, as well as DpN_{max}. Our data reveal a clearly defined daily cycle influenced primarily by road traffic activity, with a very different pattern when considering weekdays and weekends. These trends have been observed in other studies (Van Dingenen et al., 2004; Rodríguez et al., 2007). Marked peaks of $N_{13–800}$ (from less than 10,000 cm^{-3} to more than 30,000 cm^{-3}), CO (from less than 0.5 to more than 1.0 mg/m^3), NO (from less than 20 to more than 60 $\mu g/m^3$), $PM_{2.5–10}$ (from less than 10 to more than 20 $\mu g/m^3$), $PM_{2.5}$ and PM_1 (increasing between 4 and 6 $\mu g/m^3$) were recorded at traffic rush hours (7–9 h GMT in the morning and 18–21 h GMT in the evening). At the same times, DpN_{max} reached its lowest values (from >45 to <35 nm). After that, a rapid decline in atmospheric pollutants was observed, especially for N and gaseous pollutant concentrations, this being simultaneous with a slight increase in DpN_{max} values. PM levels did not always follow the same trend, remaining at similar levels or even higher after diurnal rush hours in the case of $PM_{2.5–10}$. While primary vehicle emissions affect $N_{13–800}$ and levels of gaseous pollutants, PM concentrations (especially $PM_{2.5–10}$) were strongly affected by the road dust resuspension originating from traffic flow and other PM pollution sources, including construction and demolition and wind resuspension. These large differences between the variability of PM and N concentrations allow us to recommend the measurements of both mass and number concentrations in order to better characterize the PM sources. Finally, minimum values of these parameters were obtained on Sundays, coinciding with the lowest traffic intensity in the city.

With regard to N concentrations, it is important to highlight that a $N_{13–20}$ peak can be observed between 12 and 15 h GMT, which is not being correlated with an increase in other N fractions, or primary gaseous pollutants. Furthermore, the $N_{13–20}$ peak is more evident on Saturdays and Sundays, coinciding with the lowest levels of N and PM

Table 1
Mean number (N), surface (S) and volume (V) concentrations for the period November 2003 to December 2004 measured at an urban background site in Barcelona city. The range size for N is indicated in nanometers (nm).

N	$N_{13–20}$	$N_{20–50}$	$N_{50–100}$	$N_{100–200}$	$N_{200–415}$	$N_{415–800}$	$N_{13–800}$	DpN_{max}
# cm^{-3}	2340	7480	4340	2180	414	36	16,890	39
S	$S_{13–50}$		$S_{50–100}$	$S_{100–200}$	$S_{200–415}$	$S_{415–800}$	$S_{13–800}$	DpS
$\mu m^2\ cm^{-3}$	30		62	104	80	28	304	168
V	$V_{13–50}$		$V_{50–100}$	$V_{100–200}$	$V_{200–415}$	$V_{415–800}$	$V_{13–800}$	DpV
$\mu m^3\ cm^{-3}$	0.2		1	3	5	3	12	324

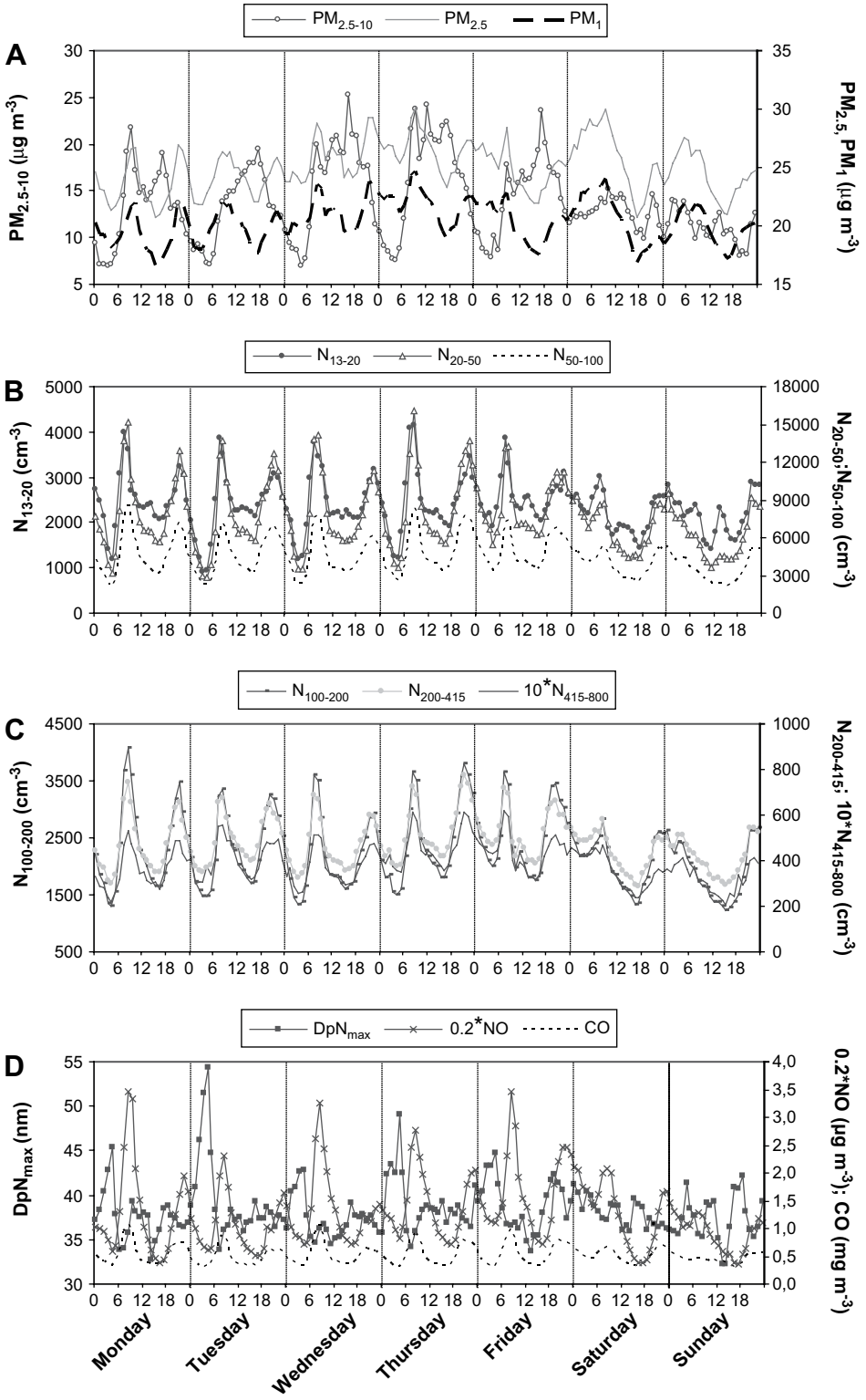

Fig. 2. Mean daily and weekly evolution of: A) $PM_{2.5-10}$, $PM_{2.5}$ and PM_1 ($\mu g\ m^{-3}$); B) N_{13-20}, N_{20-50}, N_{50-100} ($\#\ cm^{-3}$) C) $N_{100-200}$; $N_{200-415}$; $N_{415-800}$ ($\#\ cm^{-3}$) D) CO ($mg\ m^{-3}$), NO ($\mu g\ m^{-3}$) and DpN_{max} (nm).

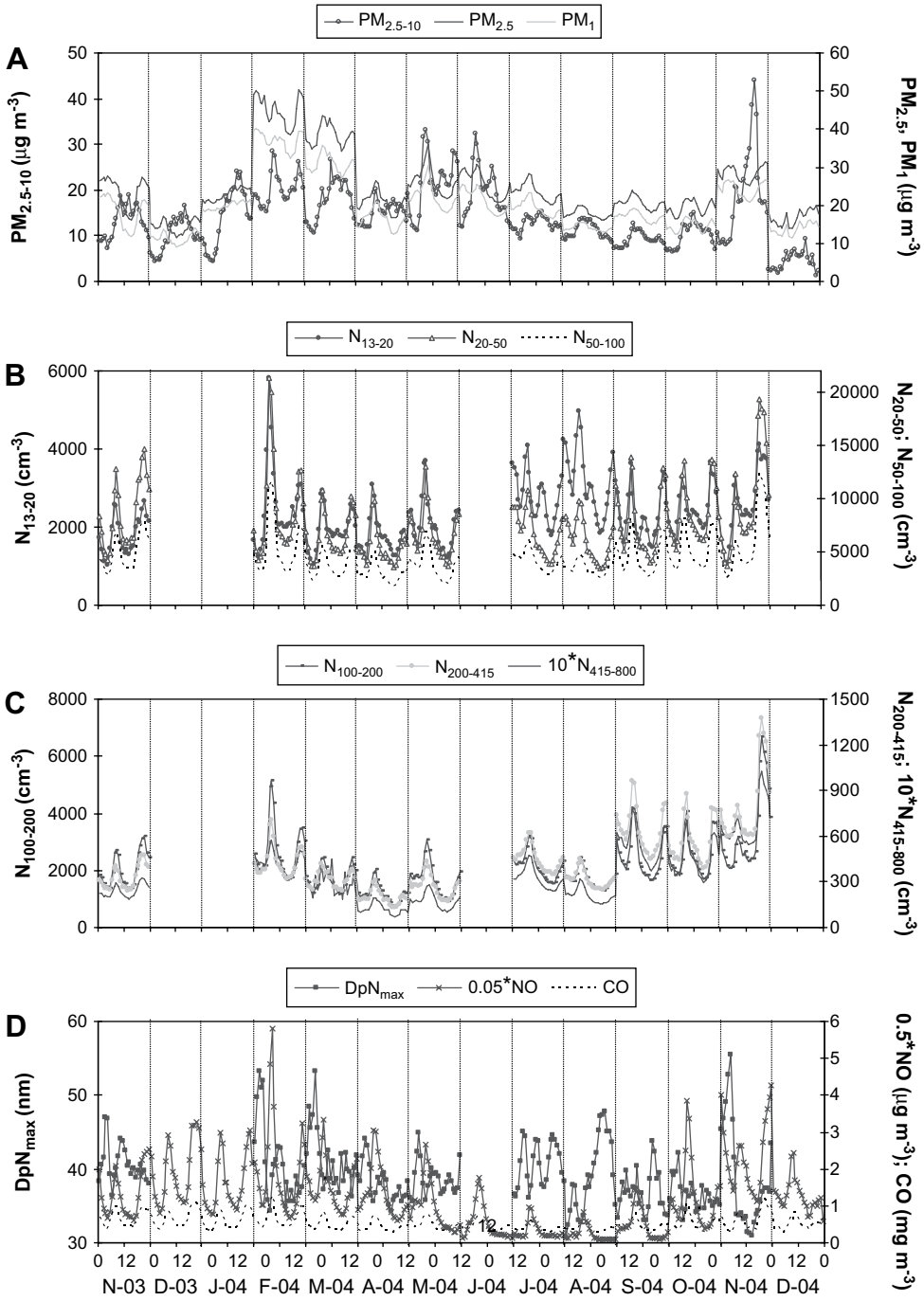

Fig. 3. Mean daily cycles per month between November 2003–December 2004 of: A) $PM_{2.5-10}$, $PM_{2.5}$ and PM_1 ($\mu g\,m^{-3}$); B) N_{13-20}, N_{20-50}, N_{50-100} (cm^{-3}); C) $N_{100-200}$; $N_{200-415}$; $N_{415-800}$ (cm^{-3}) D) CO ($mg\,m^{-3}$), NO ($\mu g\,m^{-3}$) and DpN_{max} (nm).

pollutants. This peak may be attributed to nucleation processes, in accordance to the results from Hämeri et al. (1996), who suggest that nucleation, in this case with a photochemical origin, is more favoured by lower PM pollution levels.

Viewing the weekly evolution of the different parameters it can be easily noted that a progressive increase trend was occurred from Monday to Friday (note that the minimum nocturnal values are progressively higher), with a clear decrease on Saturday and especially on Sunday. This behaviour is more evident for $PM_{2.5}$ and PM_1, as well as $N_{100-200}$, $N_{200-415}$ and $N_{415-800}$. This observation illustrates the progressive pollution of the urban atmosphere during the week, most noticeable in the accumulation mode particles (0.1–1 μm), with higher residence time in the atmosphere. As stated in previous studies carried out at this

urban site of Barcelona (Pérez et al., 2008), $PM_{2.5}$ and PM_1 fractions mainly consist of carbonaceous particles (most of them with a traffic origin) and secondary inorganic species (originating from the transformation of NO_x and SO_2 emitted by road traffic and other industrial sources), both components having a size typically in the accumulation mode. Calculating the mean values of $N_{100-800}$ between 1 and 4 h GMT we have obtained a daily increment varying from 1 to 14% from Monday to Saturday, and a marked decrease of around 26% on Sundays.

3.2. Seasonal evolution

Fig. 3 illustrates the mean daily cycle for each month of the same pollutants described above. Levels of PM, N and primary gaseous pollutants reveal in general strong seasonal variations, showing typical winter maxima and summer minima. Due to the regular contribution of the PM sources during the year, with the exception of August when a clear decrease of road traffic is detected, the observed seasonality is attributed to meteorological factors.

The winter maxima, most noticeable during important pollution episodes recorded in February–March 2004 and November 2003 and 2004, were due predominantly to low dispersive conditions and stagnant scenarios (urban pollution episodes, UP), as deduced from Fig. 4. In this Fig. 4 it should be noted that UP episodes are coincident with lower wind velocities and higher atmospheric pressure (anticyclonic stagnant scenarios). Consequently, the daily cycles of the atmospheric pollutants were intensely marked, with PM and $N_{100-800}$ peaks being superimposed upon elevated background levels. These scenarios favour the interaction between particles, and the condensation of semi-volatile species of gaseous precursors onto existing particles, resulting in clear increases of DpN_{max} (reaching mean values close to 55 nm) after traffic rush hours and during the night time. Additionally, in February and March, ten days were impacted by dusty African air masses (Fig. 4) which had a major impact on PM mass concentrations, especially on the coarser fraction, but not on N.

In April, August–October and December levels of atmospheric pollutants were at their lowest, as a consequence of

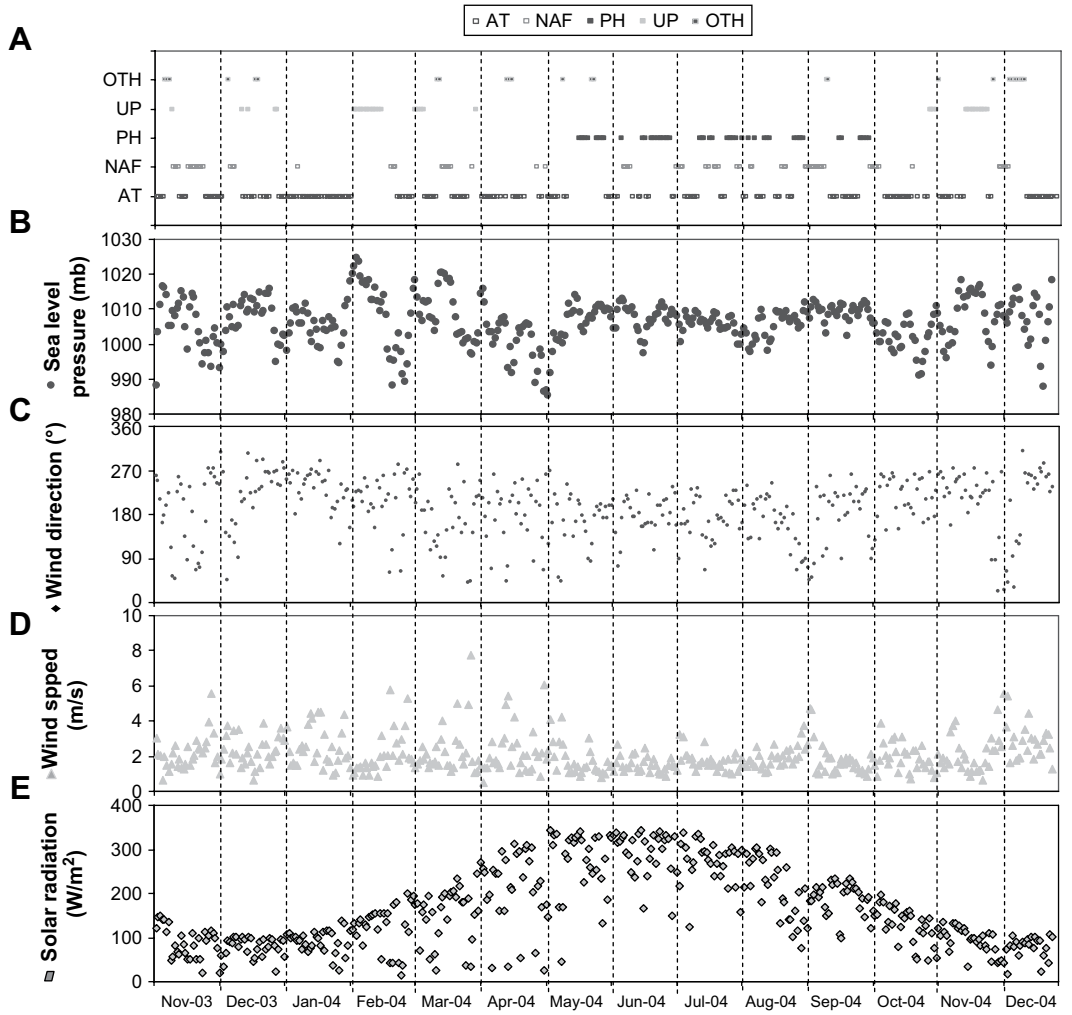

Fig. 4. Mean averages of: A) Air masses origin: AT, Atlantic advection; NAF, North African; PH, Photochemical episodes; UP, Urban pollution; OTH, Other scenarios; B) Sea level pressure (mb); C) Relatively Humidity; D) Wind velocity ($m\,s^{-1}$); E) Solar radiation ($W\,m^{-2}$).

higher wind velocities associated with intense advections (Fig. 4) and frequent rains. As explained above, in August this was attributed to a combination of reduced vehicular traffic emissions during the annual summer vacation, and the enhanced dispersive atmospheric conditions. It is important to note that, with the exception of August, the observed reduction of atmospheric pollutants affected mainly PM and $N_{100–800}$. $N_{13–100}$ shows slight variations because this fraction is more related to primary traffic emissions, contrary to $N_{100–800}$ and PM which depend in a high proportion of the interaction between the atmospheric aerosols in the urban atmosphere.

The seasonal evolution of $N_{13–20}$ was slightly different with respect to $N_{13–100}$. As stated in the previous section, a contribution of $N_{13–20}$ at midday can be attributed to photochemical nucleation. Whereas maximum winter levels of $N_{13–20}$ were observed, a secondary maximum in the summer was also detected (Fig. 3). From July to September, $N_{13–20}$ show three clear daily peaks, two coincident with the traffic rush hours, and the other neither correlated with neither NO nor CO, but coincident instead with maximum solar radiation (Fig. 4). In this period, a contribution of photochemical nucleation particles to $N_{13–20}$ is evident.

Generally, the $N_{13–800}$ morning peaks were of higher intensity than those recorded at late evening, with the exception of November 2003 and 2004, when late evening maxima were considerably higher. This observation may be attributed to the lower atmospheric dispersion during late evening traffic rush hours in this period with respect to the morning rush hours.

3.3. Aerosol events

The variability of SMA levels is highly influenced by the meteorology, as demonstrated in the previous section. To better understand variability of SMA in Barcelona under different atmospheric conditions, the most relevant meteorological scenarios were studied (Table 2 and Fig. 5).

3.3.1. Urban pollution episodes

Stagnation of air masses in Barcelona occurs with a relatively high frequency (8%, Table 2 and Fig. 4), coinciding with high surface atmospheric pressure and the absence of strong winds. Such conditions favour the accumulation of pollutants within the city, and consequently the coagulation between pre-existing particles and the condensation of semi-volatile compounds on pre-existing particles are enhanced. Table 2 summarizes the mean concentrations of N and PM during these episodes, when the proportion between ultrafine ($N_{13–100}$) particles versus $N_{13–800}$ reached its lowest values (82%). Fig. 5A illustrates the daily variability of dN/dlogDp and PM_1 during 3rd February 2004, being one of the days with higher pollution levels during the study period. After relatively low values of dN/dlogDp (low concentration of particle number but most of the particles with large diameter) during the night and maximum levels of PM_1 (the low temperatures and the high relatively humidity favour intense condensation processes over pre-existing particles, increasing the mass concentration markedly at this time), the morning traffic rush hours (from 6 h GMT) increased the dN/dlogDp values up to 60,000, with a typical size distribution peaking at around 30 nm at the beginning, reaching values close to 100 nm at 10 h GMT. After that, dN/dlogDp decreased considerably showing relatively low values until late evening, when the traffic flow increased again and a similar trend to the described for the morning rush hours was recorded. In contrast, a diminution of the PM_1 concentrations is observed from rush hours, attributable to the better dispersive atmospheric conditions.

From these data it can be deduced that during UP episodes the primary vehicle exhaust emissions clearly affect SMA levels, but the interactions between the particles (coagulation) or between particles and semi-volatile compounds (condensation) are highly favoured, with the consequent and progressive displacement of the aerosol size distribution towards the accumulation mode (Table 2 and Fig. 5A). PM and number concentrations varied inversely during this type of episodes. The UP episodes (frequent and intense in late autumn–winter) increase the $N_{13–800}$ concentrations markedly. As a consequence of these episodes the mean monthly levels recorded in November 2003 and 2004 and in February 2004 varied between 18,000 and 22,000 cm^{-3} (compared with the mean levels around 17,000 cm^{-3}).

3.3.2. Intense Atlantic advection

Advective Atlantic westerly to northwesterly winds blow across the city for around 50% of the days in a year (Table 2 and Fig. 4). This scenario is most common in autumn and spring (Fig. 4), and is occasionally coupled with rainfall. In general, this type of advection (with or without associated rains) has a cleaning effect on the urban atmosphere, resulting in the lowest PM and N levels (Table 2). To illustrate the main processes occurring during AT events, the 15th October 2004 (Friday) was selected as providing a good example of the effect of strong northwesterly winds (Fig. 5B).

Table 2
Top; mean frequency of Atlantic advection (AT), North African dust outbreaks (NAF), photochemical episodes (PH) and urban pollution scenarios (UP) recorded in Barcelona during the study period. Mean levels of N and PM in different grain sizes associated to the different meteorological scenarios. Bottom; mean values of temperature (T, °C), relatively humidity (RH, %), wind direction (WD, °), wind velocity (WV, $m\,s^{-1}$) and sea level pressure (SLP, mb).

	Frequency (days/total)	$N_{13–20}$ (# cm^{-3})	$N_{100–800}$ (# cm^{-3})	$N_{13–800}$ (# cm^{-3})	$N_{13–100}/N_{13–800}$(%)	$N_{13–20}/N_{13–800}$(%)	PM_{10} ($\mu g\,m^{-3}$)	$PM_{2.5}$ ($\mu g\,m^{-3}$)	PM_1 ($\mu g\,m^{-3}$)	T (°C)	RH (%)	WD (°)	WV ($m\,s^{-1}$)	SLP (mb)
AT	184/399	2130	13,450	15,760	85	14	35	22	18	15	63	214	2.1	1005
NAF	62/399	2400	13,660	16,230	84	15	46	31	24	19	74	138	2.4	1007
PH	50/399	3160	15,200	18,200	84	17	41	25	21	24	69	179	1.4	1007
UP	30/399	2910	20,860	25,600	82	11	57	41	35	13	72	222	1.4	1010

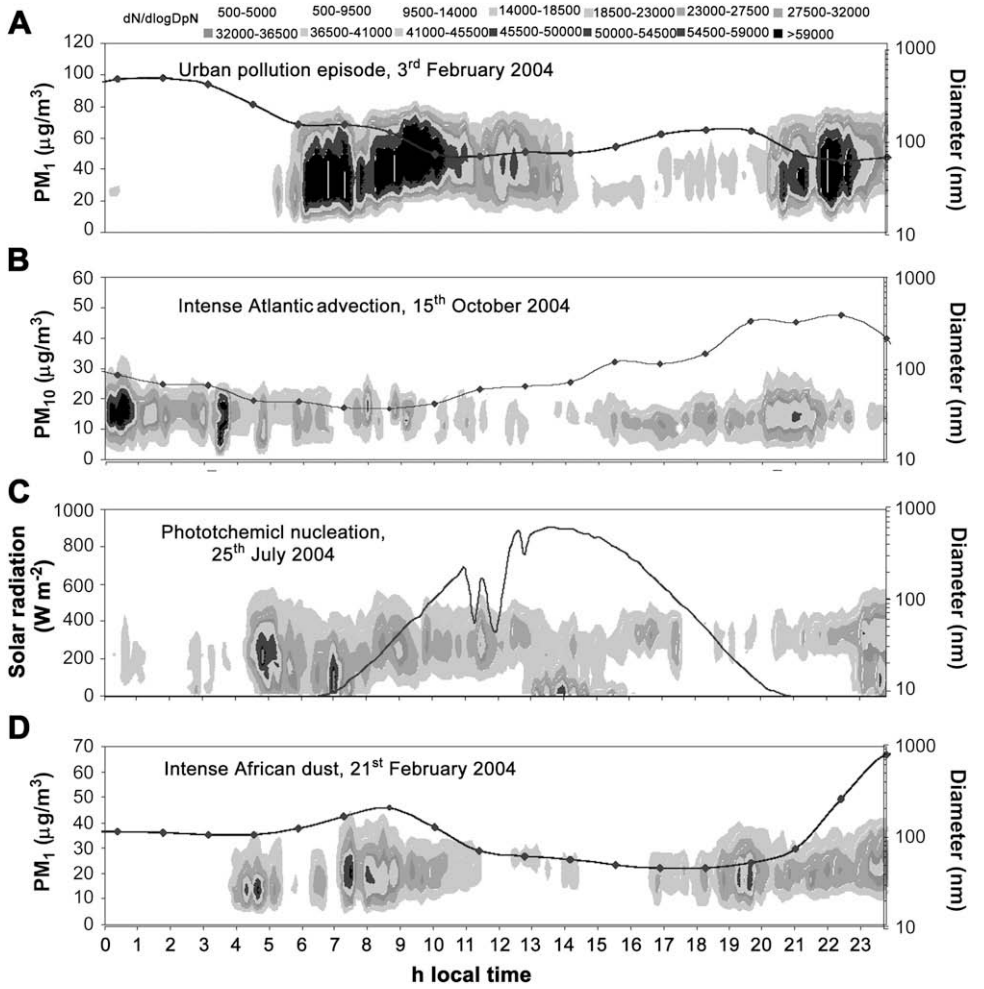

Fig. 5. Daily variability of dN/dlogDpN in Barcelona-CSIC during: A) an urban pollution episode on 3rd February 2004; B) an intense Atlantic advection on 15th October 2004; C) a photochemical nucleation event on 25th July 2004; D) an African dust outbreak on 21st February 2004.

With regard to concentration of SMA, Fig. 5B shows that dN/dlogDp presented relatively low values (<20,000), only becoming higher (up to 45,000) at rush hours and during the night period (for any reason the traffic intensity during that night was anomalously high). No evidence of particle growth was detected, but the primary vehicle emissions have a clear influence on N of ultrafine particles, as well as on PM mass.

3.3.3. *Afternoon nucleation events*

The occurrence of afternoon $N_{13–20}$ events is strongly dependent on the quantity of solar radiation and the absence of clouds. Consequently, intense PH episodes have been detected exclusively in the summer period (Table 2 and Fig. 4), even though this kind of episodes may occur along the year. As previously stated, PH episodes were of a higher intensity on Saturdays and Sundays, coinciding with the lower emissions of ultrafine particles from road traffic, which is in agreement with previous observations (Hämeri et al., 1996). As shown in Fig. 5C, an intense PH episode (DpN_{max} lower than 13 nm, contrasting with the

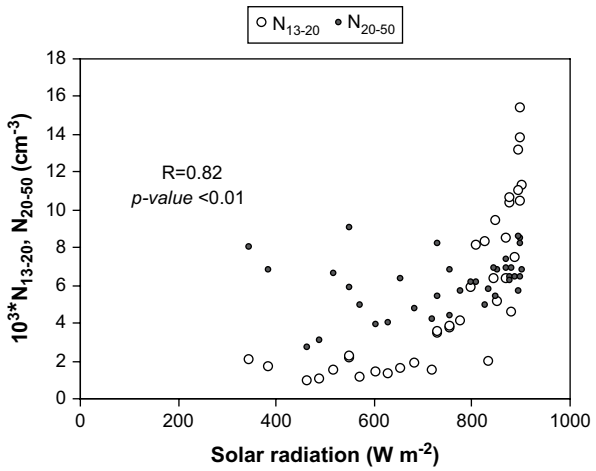

Fig. 6. Cross correlation between $N_{13–20}$ and $N_{20–50}$ (cm^{-3}) with solar radiation ($W\,m^{-2}$) from 10:00 to 16:00 h local time during an intense photochemical nucleation episode on 25th July 2004 (7 min average).

typical values around 40 nm) occurred on 25th July 2004, highly coincident with the increment of solar radiation. A considerable increment of N_{13-20} was detected when solar radiation exceeded 700 W m^{-2}, reaching values up to 15.000 cm^{-3}. On the contrary, N_{20-50} did not change when solar radiation increased (Fig. 6) because it is mostly dependent on local road traffic emissions. During this PH episode the correlation between N_{13-20} and the solar radiation was very high and significant ($R = 0.82$, p-value < 0.01).

3.3.4. African dust outbreaks

The effect of NAF episodes on PM levels in the study area is well documented (Querol et al., 2004; Escudero et al., 2006), but there is no evidence on how these episodes affect SMA levels. Mean PM levels and N in different grain sizes are presented in Table 2. Whereas mean PM levels were relatively higher during NAF episodes, N levels did not vary widely. NAF episodes occur with a higher frequency in summer, but are also detected during the rest of the year (Fig. 4). Fig. 5D shows the simultaneous variability of PM_1 and dN/dlogDpN during the most intense NAF episode recorded in the studied period, which occurred on 21st February 2004. This intense dust episode highly increased the mean daily PM_{10}, $PM_{2.5}$ and PM_1 levels up to 185, 82 and 36 μg/m^3, respectively, but no clear influence on N_{13-100} was detected due to the dominant coarse grain size of African dust, with a very low correlation between PM_{10} and N_{13-100} ($R = 0.38$, p-value $= 0.06$). Only the variability of the $N_{415-800}$ fractions (Fig. 7) was highly correlated ($R = 0.87$, p-value < 0.01) with PM_{10} (which has a natural origin during this episode), and especially with PM_1 ($R = 0.88$, p-value < 0.01). Thus, during NAF episodes we observed that the number concentration of ultrafine aerosols did not vary due to the presence of dusty African air masses. The general trends of N_{13-800} during NAF episodes are dependent on the local emissions, although a good correlation was found between PM and $N_{415-800}$, attributed to the influence of the mineral dust particles.

3.4. Correlation between number and mass concentrations

The cross correlation between PM mass and number concentrations increases with the particle size. Fig. 8 shows such correlation between PM_1 and different N size fractions: N_{13-20} (nucleation particles), N_{20-200} (mainly primarily emitted particles), $N_{200-415}$ and $N_{415-800}$ (accumulation mode particles). No correlation between N_{13-20} and PM_1 has been found ($R = 0.11$), probably due to the major occurrence of intense nucleation events (contributing to N_{13-20}) during low atmospheric pollution periods (with high PM_1 levels). A positive correlation has been observed between N_{20-200} and PM_1 ($R = 0.33$), although a higher data scatter was observed. The correlation with PM_1 increased for $N_{200-415}$ ($R = 0.37$) and $N_{415-800}$, ($R = 0.54$) although relatively high data scattering was also observed. The p-value obtained for the nucleation mode size range was 0.07, but was <0.01 for the other N size ranges. These results indicate that the correlation between N_{20-800} and PM_1 is statistically significant, in spite of the relatively high data scatter observed.

Thus, the grain sizes contributing a major proportion of the PM_1 mass concentration were $N_{200-415}$ and $N_{415-800}$ (accumulation mode particles), corroborating that number and mass concentrations are not always affected by the same sources and atmospheric processes.

4. Summary and conclusions

The results of our extensive measurements of aerosol mass (PM) and number (N) concentrations of grain size distribution carried out in Barcelona (Spain) indicate that while PM levels were relatively higher than in other urban European cities, mean levels of N were in the usual range measured in similar urban environments, with around 85% of N_{13-800} being ultrafine particles.

As expected, SMA levels depend strongly on the primary and secondary emissions from road traffic. Nevertheless, the meteorology exerts a high influence on the seasonal variability of PM and SMA levels. Thus, both PM and N levels tend to increase in winter and decrease in summer, when better dispersive atmospheric conditions are present (favoured by stronger sea breezes). In the case of August the decrease of N is also favoured by the reduction of road traffic as consequence of holiday period. The finest fraction (N_{13-20}) showed both winter and summer maxima, the

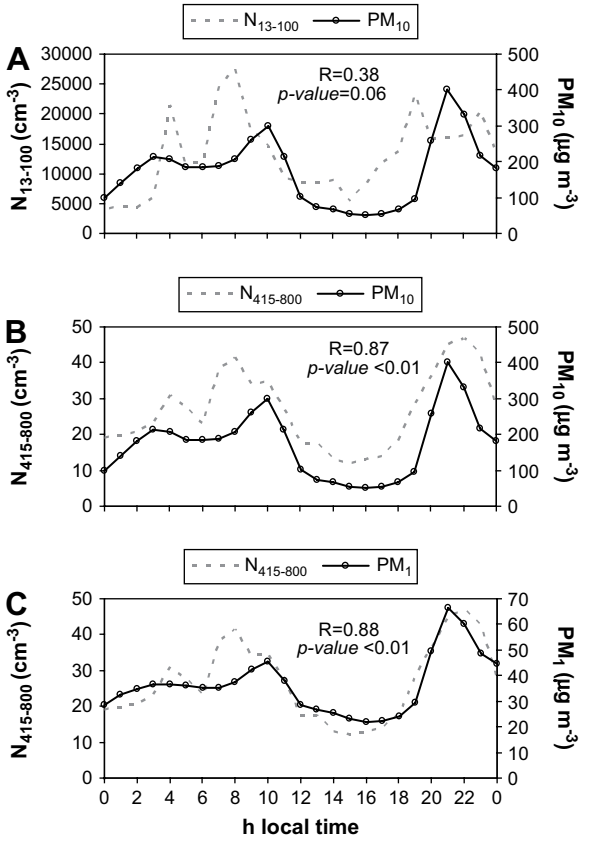

Fig. 7. Daily variability of: A) N_{13-100} (cm^{-3}) and PM_{10} (μg m^{-3}), B) $N_{415-800}$ (cm^{-3}) and PM_{10} (μg m^{-3}); C) $N_{415-800}$ (cm^{-3}) and PM_1 (μg m^{-3}), during an African dust episode occurred on 21st February 2004.

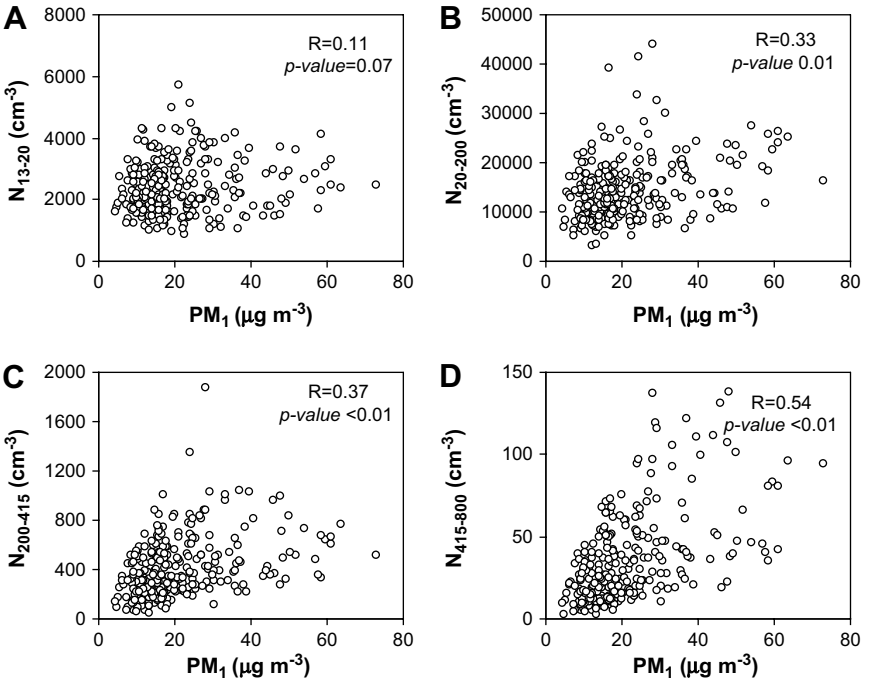

Fig. 8. Cross correlation plots between mean daily concentrations of N_{13-20}; N_{20-200}, $N_{200-415}$ and $N_{415-800}$ (cm^{-3}) and mean daily concentrations of PM_1 ($\mu g\ m^{-3}$).

latter being attributed to the contribution of photochemical nucleation particles.

The variability of N levels depending on the most typical atmospheric scenarios revealed that UP episodes were characterized by high N_{13-800} concentrations (25,600 cm^{-3}), but also by an intense interaction between aerosols and/or semi-volatile compounds (agglomeration and condensation processes favouring the growth of particle size and mass giving rise to high levels of N in the accumulation mode). During intense Atlantic advections slightly low N_{13-800} levels (15,800 cm^{-3}) were recorded. These intense advections did not promote the interaction between aerosols and/or gaseous pollutants (thus, N and PM levels varied simultaneously). Photochemical episodes mainly occurred after midday in summer, during the maximum intensity of solar radiation, with high N_{13-20} concentrations (3150 cm^{-3}). African dust episodes did not decisively influence the number concentration of N_{13-800} (a mean value of 16,200 cm^{-3} was obtained), with only the $N > 400$ fraction being highly influenced by these natural PM episodes.

The cross correlation between number and mass concentrations showed a relatively poor agreement, especially between variability of levels of PM_1 and the nucleation mode $N < 20$ ($R = 0.11$). Only the aerosol number concentration of the accumulation mode was highly correlated with the PM_1 mass, but with an elevated data scattering ($R = 0.37$–0.54). In Barcelona, aerosol number and mass concentrations were affected by different sources or atmospheric processes. The measurement of the aerosol number is highly recommended in order to understand local urban aerosol emissions, while mass concentrations are necessary to detect and quantify the contribution of other sources such as road dust, or long distance transport episodes such as African dust events. Consequently, in order to better monitor the impact of different sources of atmospheric particulate matter and atmospheric processes on urban air quality, both parameters mass and number concentrations should be simultaneously monitored.

This study (the first of this type in Spain) reveals that the concentrations of the SMA in Barcelona (Southern Europe) are at the same range that those registered at many other urban cities in Europe. This contrasts with that the comparison of PM_{10} concentrations, considerably higher in Barcelona with respect to Central, Western and Northern Europe. One of the most interesting findings of this study is the occurrence of intense photochemical nucleation episodes at this urban site, probably enhanced by the intense insolation and the high relatively humidity.

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