

# Ultrafine particle formation in the inland sea breeze airflow in Southwest Europe

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**Abstract.** Studies on ultrafine particles (diameter < 100 nm) and air quality have mostly focused on vehicle exhaust emissions and on new particle formation in “clean” ambient air. Here we present a study focused on the processes contributing to ultrafine particle concentrations in a city (Huelva, SW Spain) placed close to a coastal area where significant anthropogenic emissions of aerosol precursors occur. The overall data analysis shows that two processes predominantly contribute to the number of particles coarser than 2.5 nm: vehicle exhaust emissions and new particle formation due to photo-chemical activity. As typically occurs in urban areas, vehicle exhaust emissions result in high concentrations of black carbon (BC) and particles coarser than 2.5 nm (N) during the morning rush hours. The highest N concentrations were recorded during the 11:00–17:00 h period, under the sea breeze regime, when low BC concentrations were registered and photochemical activity resulted in high O<sub>3</sub> levels and in new particle formation in the aerosol precursors’ rich inland airflow. In this period, it is estimated that about 80% of the number of particles are linked to sulfur dioxide emissions. The contributions to N of “carbonaceous material and those compounds nucleating/condensing immediately after emission” and of the “new particle formation processes in air masses rich gaseous precursors (e.g. SO<sub>2</sub>)” were estimated by means of a relatively novel method based on simultaneous measurements of BC and N. A comparison with two recent studies suggests that the daily cycles of “new particle forma-

tion” during the inland sea breeze is blowing period seem to be a feature of ultrafine particles in coastal areas of Southwest Europe.

## 1 Introduction

Urban air quality impairment by atmospheric nano-sized particles is becoming a topic of great interest in the atmospheric and environmental sciences. A growing volume of scientific evidences shows that exposure to ultrafine particles (diameter < 100 nm) results in harmful effects on human health (Araujo and Nel, 2009). Because deposition in the respiratory system of inhaled ultrafine particles is governed by diffusional processes, it is believed that ultrafine particle translocation within the human body is dependent on particle size, in such a way that the smallest ultrafine particles (e.g. < 5 nm) mostly deposit in the nasopharyngeal region, whereas larger ultrafine particles (≥ 20 nm) mostly reach the alveoli and enter the bloodstream (ICRP, 1994; Oberdörster et al., 2004). Many medical studies are currently focusing on translocation and the effects of solid ultrafine particles (rather than on liquid or semi-volatile aerosols). In a study with rats, Oberdörster et al. (2004) demonstrated that inhaled solid ultrafine particles deposited on the olfactory mucosa reach the central nervous system via the olfactory nerve. Translocation of inhaled ultrafine particles from the lungs to the liver and accumulation in the liver has been documented as occurring in a matter of a few hours (Oberdörster et al., 2002). Recent laboratory studies have elucidated the mechanism by which exposure to ultrafine particles enhances atherosclerosis and



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cardiovascular ischemic events (Araujo et al., 2008). This may account for the association between “ambient particulate matter pollution” and “increased morbidity and mortality due to cardiovascular diseases” observed in epidemiological studies (Analitis et al., 2006). Chemical composition is also relevant; some ultrafine particles are constituted by potentially carcinogenic compounds (such as PAHs linked to soot; Morawska and Zhang, 2002). Given that these adverse effects on human health and because ultrafine particles are not properly quantified in terms of PM<sub>10</sub> and PM<sub>2.5</sub> (the current metrics in air quality standards), there is open debate on the necessity to regulate concentrations of ultrafine particles in ambient air (Second Position Paper on PM, 2004; COST 633 Report, 2009).

Ultrafine particles typically account for 80–90% of the total particle number concentration in urban air (Wehner and Wiedensohler, 2003; Rodríguez et al., 2007; Mejía et al., 2008). For this reason, many studies on ultrafine particles in urban air have been based on measurements of total number concentrations of particles coarser than 10 nm (e.g. Harrison and Jones, 2005) or 3 nm (e.g. Shi et al., 1999). Most studies attribute two main origins to these urban particles (e.g. Dunn et al., 2004; Morawska et al., 2008):

- *Primary vehicle exhaust emissions.* These particles show bimodal size distribution, with a nucleation (<30 nm) and a soot mode (50–100 nm). In general, it is believed that binary H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> nucleation and subsequent particle growth by condensation of sulphate and/or hydrocarbons during the dilution and cooling of the exhaust emissions plays an important role in the nucleation mode (Burtcher, 2005; Arnold et al., 2006). It has also been proposed that the formation mechanism may change depending on the exhaust after-treatment system, fuel composition, lubricant oil and environmental parameters (De Filippo and Maricq, 2008; Rönkkö et al., 2007; Du and Yu, 2008; Heikkilä et al., 2009). A fraction of the nucleation mode material is semi-volatile and its formation rate depends on the dilution conditions and on the temperature and relative humidity of the ambient air (Casati et al., 2007). The soot mode is made up of elemental carbon, absorbed organic material and some other trace elements formed in the engine and directly emitted in the solid phase (Burtcher, 2005; Rose et al., 2006).
- *New particle formation in ambient air.* This process is generally linked to nucleation and subsequent cluster/particle growth by condensation of photo-oxidized vapors (Morawska et al., 2008; Dunn et al., 2004). The cluster activation theory proposes that new particle formation occurs in two (not necessarily coupled) steps (Kulmala and Kerminen, 2008): i) nucleation of an initial cluster (the nucleation process itself), and ii) activation of these clusters resulting in particle growth to a

detectable diameter. It has been observed that the clusters necessary for the initial steps seem to be always present in the atmosphere (Kulmala et al., 2005) and that nucleation of sulfuric acid gas molecules plays a key role in the formation of such stable clusters (0.5–1.5 nm size; Kulmala et al., 2006). Thus, the so-called new particle formation would occur when these clusters are activated and grow to detectable sizes. Sipilä et al. (2010) detected formation of 1.5 nm particles at atmospherically relevant sulfuric acid concentrations. It is believed that species involved in the nucleation step might not necessarily be the same as those involved in cluster/particle growth by condensation, and that nucleation (of clusters) and growth could be decoupled steps (Kulmala and Kerminen, 2008).

Our knowledge of ultrafine particles and urban air quality has experienced a significant increase in the last decade. However, some issues require more in-depth investigation. Some examples:

- Most studies have focused on vehicle exhaust emissions and on new particle formation in “clean” ambient air (e.g. references above). However, the contribution of other types of emission sources, such as plumes of particle precursors (e.g. industrial, ships, etc.), to ultrafine particle concentrations in ambient air has not been investigated in depth, even though it is well known that these activities may release important gaseous precursors. For example, Stanier et al. (2004) observed that nucleation was associated with the presence of SO<sub>2</sub> and with radiation intensity.
- The influence of meteorology and the dispersion conditions of such aerosol precursor plumes on ultrafine particle formation in ambient air requires more in-depth investigation. In contrast, ultrafine particle formation during the cooling of vehicle exhaust emissions and their dilution and transport from a canyon street to the urban background has been widely studied (e.g. Wehner et al., 2002). Previous studies have shown that the development of coastal breezes in Southern Europe exerts a strong influence on the formation of ozone and secondary particles on a regional level (Millán et al., 2002; Rodríguez et al., 2004); however the influence of this meteorological scenario on the formation of ultrafine particles is unknown.
- There is a lack of techniques/methodologies for quantifying the sources and processes contributing to ultrafine particle concentrations in urban ambient air. A few attempts have been made. By applying receptor modeling techniques to a database of daily average values of PM<sub>2.5</sub> chemical composition and particle size distribution, Pey et al. (2009) concluded that “vehicle exhaust emissions” and “new particle formation in ambient air”

accounted for 65% and 24% of the 10–100 nm particles, respectively, in Barcelona. By using 10-min average data of black carbon and number of particles concentrations, Rodríguez and Cuevas (2007) estimated that ultrafine particles in Santa Cruz de Tenerife city mostly came from vehicle exhaust emissions during the morning rush hours, whereas about 70% of these ultrafine particles were linked to new particle formation in ambient air during the afternoon.

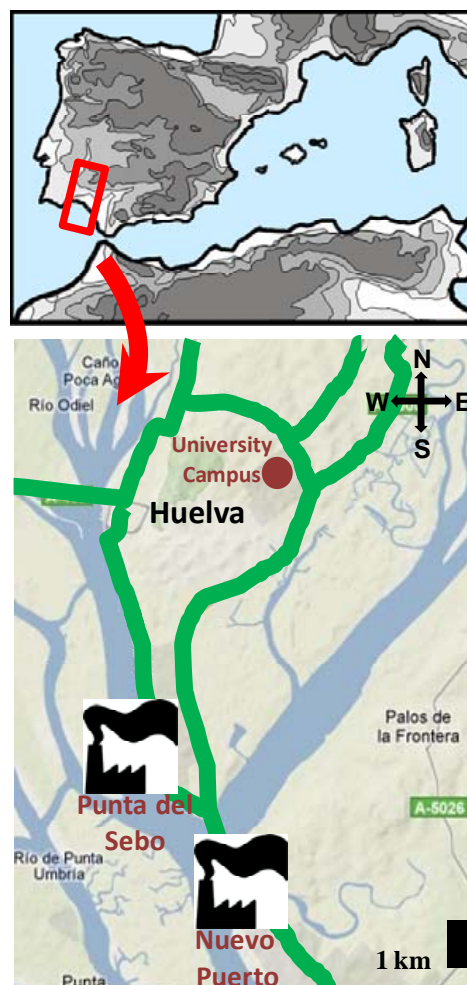
In this paper we present a study of ultrafine particles and industrial emissions of gaseous precursors. The objective is to identify the sources and processes contributing to ultrafine particle concentrations in ambient air downwind of coastal industrial emissions. The results show that these emissions coupled with suitable meteorological conditions typical of coastal areas give rise to high concentrations of ultrafine particles. These results show that “non-vehicle exhaust emission” sources may also contribute significantly to ultrafine particles in urban ambient air.

## 2 Methodology

### 2.1 Study area

The city of Huelva (around 140 000 inhabitants) is located in the south-western part of the autonomous region of Andalusia in Spain (Fig. 1). The city spreads out over a flat area in the southern end of the “V”-shaped confluence between the Odiel and Tinto rivers. The city is surrounded by a ring road that allows road-traffic to connect the city with motorways (Fig. 1).

In addition to the typical urban vehicle exhaust emissions, aerosol precursors are emitted at the south of the city. These emissions are related to industrial activities (in Punta del Sebo and Nuevo Puerto industrial areas; Fig. 1) and to maritime transport (ship). According to the European Pollution Emission Register (EPER; <http://eper.ec.europa.eu/eper/>) and to previous field studies (Querol et al., 2002; Alastuey et al., 2006; Sánchez de la Campa et al., 2007, 2008, 2009; Sánchez-Rodas et al., 2008; De la Rosa et al., 2010; Fernández-Camacho et al., 2010), the most significant industrial activities in Punta del Sebo include: i) a Cu-smelter plant whose  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ , As, Sb, Pb, Zn and Sn emissions are well documented, and ii) phosphoric acid production plants, which are a source of atmospheric  $\text{NH}_4^+$  and Na phosphate, phosphoric acid, sulfuric acid and sodium silicate. Special attention is paid to the Cu-smelter plant, given that it is a very significant source of  $\text{SO}_2$  and heavy metals (Fernández-Camacho et al., 2010). According to the above information sources, the most significant air pollutant emissions in Nuevo Puerto occur in a crude oil refinery resulting in emissions of volatile hydrocarbons,  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ , Ni, V and particulate matter. Finally, ship emissions may occur



**Fig. 1.** Map of Huelva and the surroundings. Green lines indicate main roads and motorways around Huelva city. The two industrial areas (Punta del Sebo and Nuevo Puerto) of Huelva are highlighted.

in the harbor and in the bay of Huelva. This is a transit region for ships sailing to/from the Strait of Gibraltar, which  $\sim 80000$  ships pass through every year (Viana et al., 2009). In all these cases sea-to-land winds result in the inland transport of aerosols and their precursors (e.g.  $\text{SO}_2$ ).

The dispersion and transport of air pollutants in this area are highly influenced by the topographic setting (Mantilla, 2007). At night, the wind mostly blows from the north, associated with the channeling of airflows along the Guadalquivir basin, prompted by the synoptic Azores anticyclone. During daylight, southern airflows linked to thermally driven breezes predominate. In this period, the inland entry of coastal breeze coupled with the airflow channeled along the river pathway, favor the entry of industrial plumes from the Punta del Sebo and Nuevo Puerto areas to the city centre. This sea breeze blowing inland is typically associated with an increase in ozone concentrations (Millán et al., 2002).

## 2.2 Measurements

Data on particle number, black carbon and PM<sub>10</sub> concentrations, gaseous pollutant concentrations (NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub>, among others) and meteorological parameters were collected at the urban background air pollution research station located at the University Campus. This site is situated on the northeast side of the city, 7 km from Punta del Sebo and 14 km from Nuevo Puerto industrial areas. The closest roads, Avenida Andalucía and Avenida Fuerzas Armadas lie about 500 and 1000 m to the west and the east of the measurement site, respectively (Fig. 1). The current study is based on data collected between April 2008 and September 2009. Data availability in this period is of about 70% for particle number, 95% for black carbon, 80% for PM<sub>10</sub>, 85% for NO<sub>x</sub>, 85% for SO<sub>2</sub>, 87% for O<sub>3</sub> and 100% for radiation, wind speed, wind direction, temperature and relative humidity.

### 2.2.1 Particles

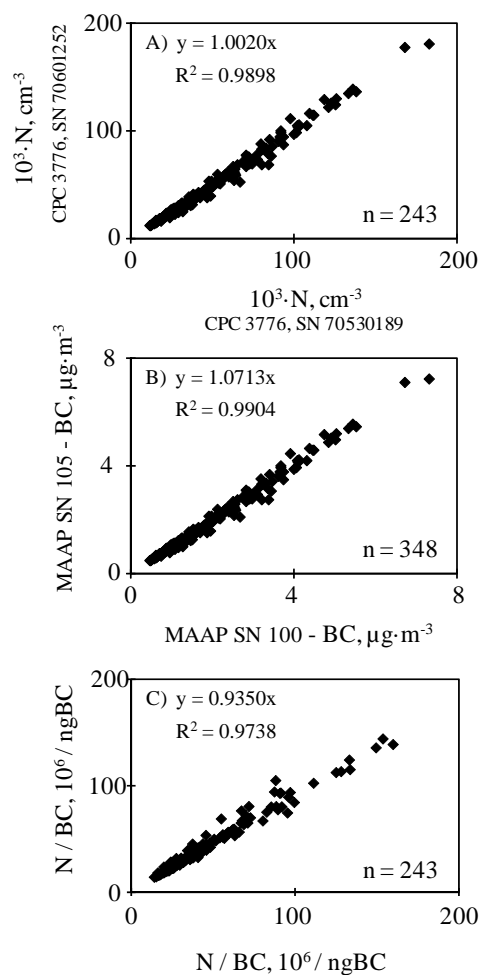
Number concentration of particles was monitored using an Ultrafine Condensation Particle Counter (UCPC, TSI™), model 3776. According to the manufacturer, this instrument detects particles coarser than 2.5 nm. Experimental measurements performed by Hermann et al. (2007) have shown that the 50% counting efficiency for these instruments is reached at diameters ( $d_{50}$ ) between 3 and 4 nm. The CPC unit used in this study (SN 70530189) was inter-compared with other unit (SN 70601252) of the same model at the beginning of the campaign. Results show a high linearity between the two instruments and that the differences were of about 0.2% for 10 min averaged data (Fig. 2a).

The instrument records data averaged at 1-min intervals. It was operated in high flow mode (1.5 l/m) to minimize diffusion losses.  $N$  is considered representative of the ultrafine particle concentration. This is supported by previous studies that showed that the number of particles with size 10–100 nm typically accounts for 80–90% of the total number concentrations in urban air (Wehner and Wiedensohler, 2003; Rodríguez et al., 2007).

Concentrations of black carbon particles (BC) smaller than 10 μm were monitored by placing a PM<sub>10</sub> impactor in the inlet of a Multi-Angle Absorption Photometer (MAAP) (Thermo™, model Carusso 5012). BC concentrations were determined using the absorption coefficient measurements at  $\lambda = 630$  nm ( $\sigma_{ap}$  in Mm<sup>-1</sup> units) taken with the MAAP by applying Eq. (1) (Petzold and Schönlinner, 2004):

$$BC(\mu\text{g m}^{-3}) = \sigma_{ap}(\text{Mm}^{-1}) / \sigma(\text{m}^2 \text{g}^{-1}) \quad (1)$$

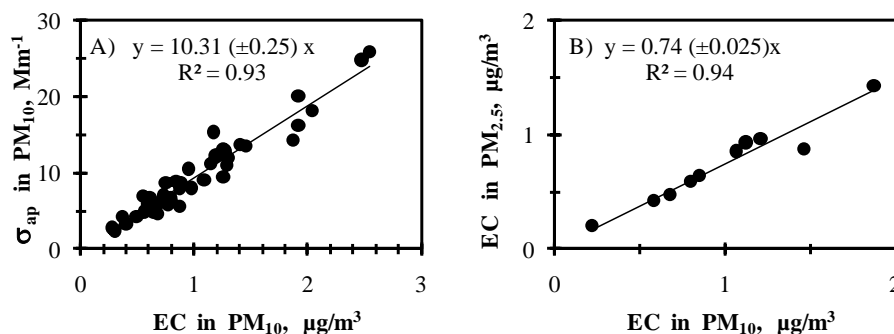
where  $\sigma$  is the “specific aerosol absorption coefficient” (expressed in m<sup>2</sup>/g units). In order to determine “ $\sigma$ ”, samples of PM<sub>10</sub> particles were collected in a high volume (68 m<sup>3</sup>/h) sampler. In these PM<sub>10</sub> samples, elemental carbon (EC) concentrations were determined by analysis in the laboratory. These were performed by means of the Thermo Op-



**Fig. 2.** Inter-comparison between the 10 min averaged data recorded with two CPCs model 3776, two MAAPs and the N/BC ratio recorded with these instruments. Data plotted in Y-axis were collected with the instruments (CPC SN70530189, MAAP SN 105) used in this study.

tical Transmittance technique (Birch and Cary, 1996) using a Sunset Laboratory™ OC-EC analyzer and the default temperature steps of the EUSAAR2 program. A parallel PM<sub>2.5</sub> sampling was occasionally performed to determine the PM<sub>2.5</sub>/PM<sub>10</sub> ratio for BC. The MAAP used in this study (SN 105) was also inter-compared with other MAAP instrument at the beginning of the campaign (Fig. 2b). The N/BC ratios measured with these instruments were also inter-compared (Fig. 2c).

Concentrations of PM<sub>10</sub> particles were determined by means of a beta attenuation monitor and a sampler for collecting PM<sub>10</sub> samples on filter media. Daily average gravimetric PM<sub>10</sub> concentrations were determined by filter weighing after conditioning (20 °C and 50% RH). Gravimetric equivalent hourly average PM<sub>10</sub> concentrations were determined by multiplying the PM<sub>10</sub> readings of the beta monitor



**Fig. 3.** (A) absorption coefficient  $\sigma_{ap}$  versus EC concentrations in  $PM_{10}$  particles, (B) BC in  $PM_{10}$  versus BC  $PM_{2.5}$ .

by the “correction factor” required to take into account losses due to volatilization in the beta instrument. This was done by following the EU standardized procedure (EC Working Group on Particulate Matter Report, 2002).

### 2.2.2 Additional data

The following complementary measurements were performed: i) concentrations of  $SO_2$ ,  $NO_x$  and  $O_3$  were monitored using standard procedures following the reference methods of the European air quality directives (2008/50/EC), ii) road-traffic intensity (number of vehicles  $\cdot$  hour $^{-1}$ ) was measured on the two main roads at each side of the measurement site, iii) meteorological parameters (wind speed and direction, temperature, relative humidity, pressure and global radiation).

## 3 Results and discussion

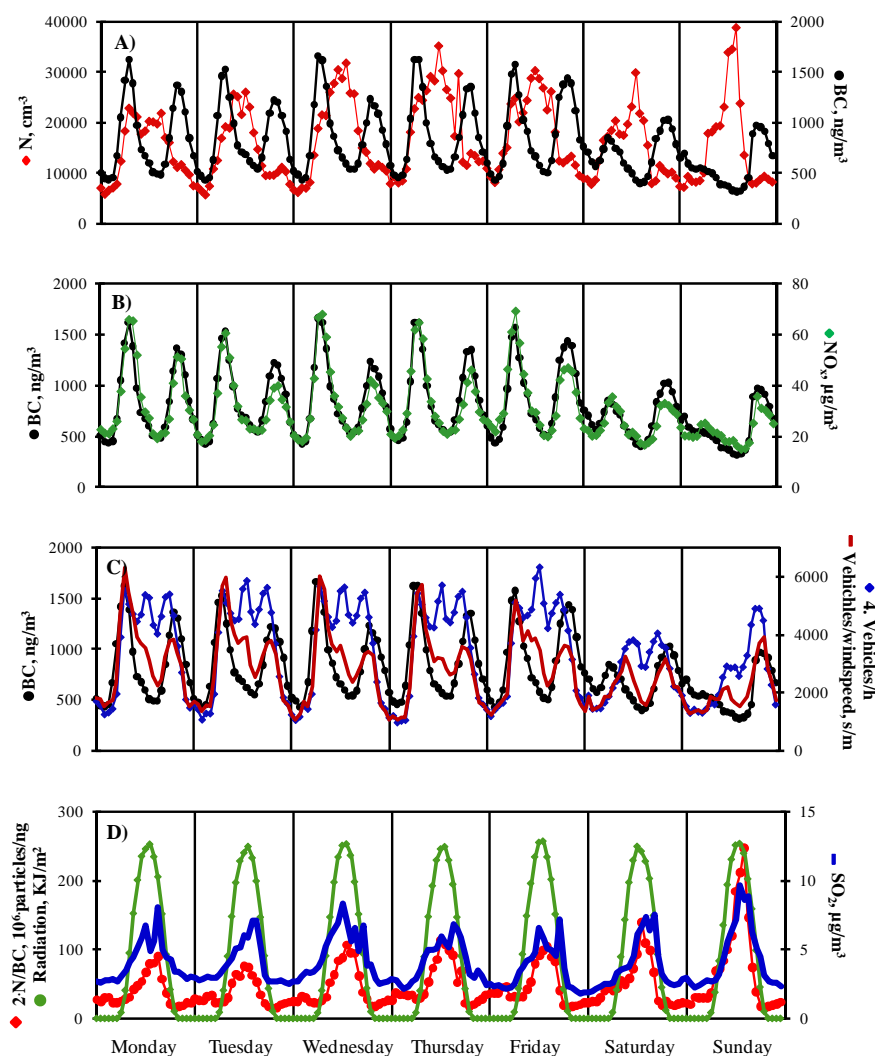
### 3.1 Absorbing aerosols

The specific aerosol absorption coefficient  $\sigma$  (expressed in  $m^2/g$  units) was determined by comparing the absorption coefficient  $\sigma_{ap}$  measured by the MAAP with the elemental carbon (EC) concentrations determined by the Sunset analysis of the  $PM_{10}$  samples. An average value of  $\sigma = 10.31 \pm 0.25 m^2/g$  was obtained (Fig. 3a). This  $\sigma$  value is within the range of those typically observed in previous studies ( $2\text{--}25 m^2 g^{-1}$ ; Bond and Bergstrom, 2006). Because of the low  $\sigma$  values typically associated with other potentially absorbing species, such as mineral dust ( $0.01\text{--}0.02 m^2 g^{-1}$ ; Alfaro et al., 2004) or organic aerosols (e.g. humic-like substances  $\sigma \sim 0.03 m^2 g^{-1}$ ; Hoffer et al., 2006), and because of the high correlation observed between absorption coefficient and nitrogen oxides during the morning rush hours (Fig. 4b, discussed below), we assume that the measured absorption coefficient is entirely due to absorption by EC. Observe in Fig. 3b that about the 75% of the EC mass in  $PM_{10}$  occurs in the fine ( $PM_{2.5}$ ) fraction.

### 3.2 Regular daily evolution

Figure 4 shows the hourly average values for particle number  $N$  and black carbon BC concentrations, several gaseous pollutants ( $NO_x$  and  $SO_2$ ) and the road-traffic intensity for each day of the week. The high correlation between BC,  $NO_x$  and “road-traffic intensity/wind speed” ratio (all of them showing high values during the morning rush hours of working days) indicates that a predominant fraction of these pollutants is linked to vehicle exhaust emissions. This is also evidenced in the working-days-to-weekend change in the BC and  $NO_x$  daily evolution. The daily evolution of  $N$  is somewhat different to that of BC. The abrupt morning increase in road-traffic intensity and in  $N$  evidence the significant influence of vehicle exhaust emissions on the ultrafine particle concentrations in this period. In contrast, the decrease observed in the “road-traffic intensity/wind speed” ratio and in BC and  $NO_x$  concentrations after the morning rush hours (Fig. 4b and c) is not observed in  $N$ . This suggests that other sources (not linked to BC and  $NO_x$  emissions) and/or processes are actively contributing to  $N$  during the central hours of daylight. The correlation between the daily evolution of the  $N/BC$  ratio,  $SO_2$  and solar radiation suggests that this additional mechanism providing ultrafine particles during the noon-afternoon period may be related to new particle formation in the  $SO_2$  downwind of the industrial plumes that reach the measurement area during the period when the sea breeze is blowing inland (Fig. 4d).

Most of studies on ultrafine particles in urban air have been based on measurements of particles  $>10$  nm. In European cities, these particles typically exhibit mean concentrations within the range  $15\,000\text{--}30\,000 cm^{-3}$  (Ruuskanen et al., 2001; Van Dingenen et al., 2004; Puustinen et al. 2007; Rodríguez et al., 2007; Putaud et al., 2010). Putaud et al. (2010) observed a clear increase in particle number when moving from rural background to urban background and kerbsides; moreover, no differences in the rural background throughout Europe were observed.



**Fig. 4.** Hourly average values of particles (N and BC) and gaseous pollutant ( $\text{NO}_x$  and  $\text{SO}_2$ ) concentrations, and of road-traffic intensity (number of vehicles/hour), the road-traffic intensity/wind speed ratio, of the N/BC ratio and solar radiation, for every day of the week.

We have made an effort to compare mean concentrations of  $>2.5$  nm particles in Huelva with those recorded in other cities; however data on these types of particles are still scarce. The mean value of the  $\geq 2.5$  nm particle number concentrations recorded in Huelva is ( $\sim 22\,000\text{ cm}^{-3}$ ) within the range of those typically recorded in other urban background sites ( $\sim 20\,000\text{ cm}^{-3}$  in Santa Cruz de Tenerife city and  $\sim 22\,000\text{ cm}^{-3}$  in Pittsburg for  $\sim 3$  nm particles; Rodríguez and Cuevas, 2007; Stanier et al., 2004) and much lower than those recorded in street canyons and road-traffic sites ( $\sim 64\,000\text{ cm}^{-3}$  in Leipzig and  $170\,000\text{ cm}^{-3}$  in Birmingham for  $\geq 3$  nm particles; Wehner et al., 2002; Shi et al., 1999). One of the most important features of the  $\geq 2.5$  nm particles in Huelva is their regular daily evolution. In most urban areas, the number of  $\geq 3$  nm particles reaches a maximum mostly during the morning rush hours (e.g. Leipzig, Santa Cruz de Tenerife) due to vehicle exhaust emissions. In

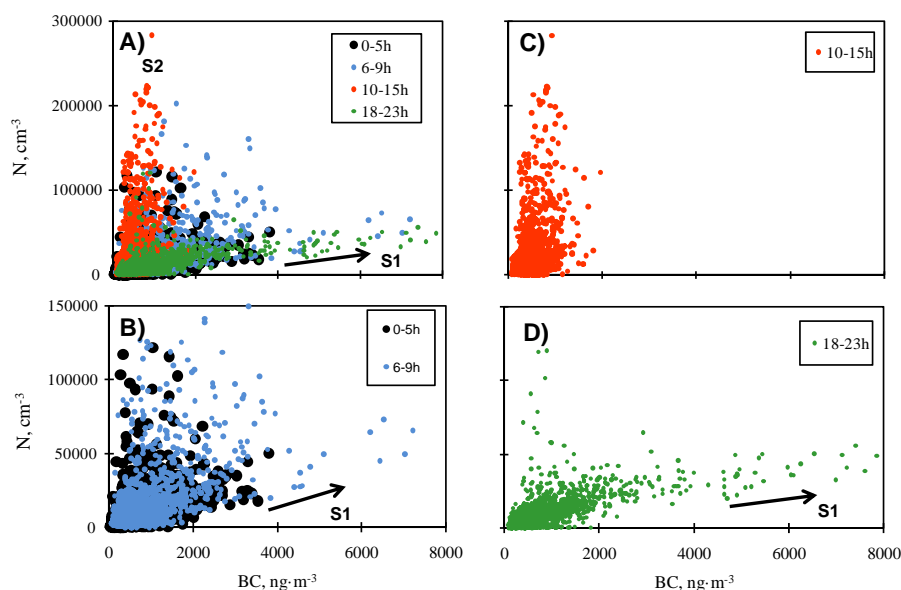
contrast, the maximum concentrations of  $\geq 2.5$  nm particles in Huelva are reached during the afternoon (12:00–14:00 h).

### 3.3 Relationship between particle number and black carbon concentrations

Correlations between particle number and black carbon concentrations are regularly observed in urban air due to vehicle exhaust emissions (Fruin et al., 2004; Rodríguez et al., 2007; Rodríguez and Cuevas, 2007). These correlations are also observed in Huelva.

We have analyzed the relationship between the particle number N and black carbon BC concentrations following the methodology described by Rodríguez and Cuevas (2007). Figure 5 shows the N versus BC scatter plots for different periods of the day (00:00–05:00 h, 06:00–09:00 h, 10:00–15:00 h and 18:00–23:00 h). It can be observed that at any





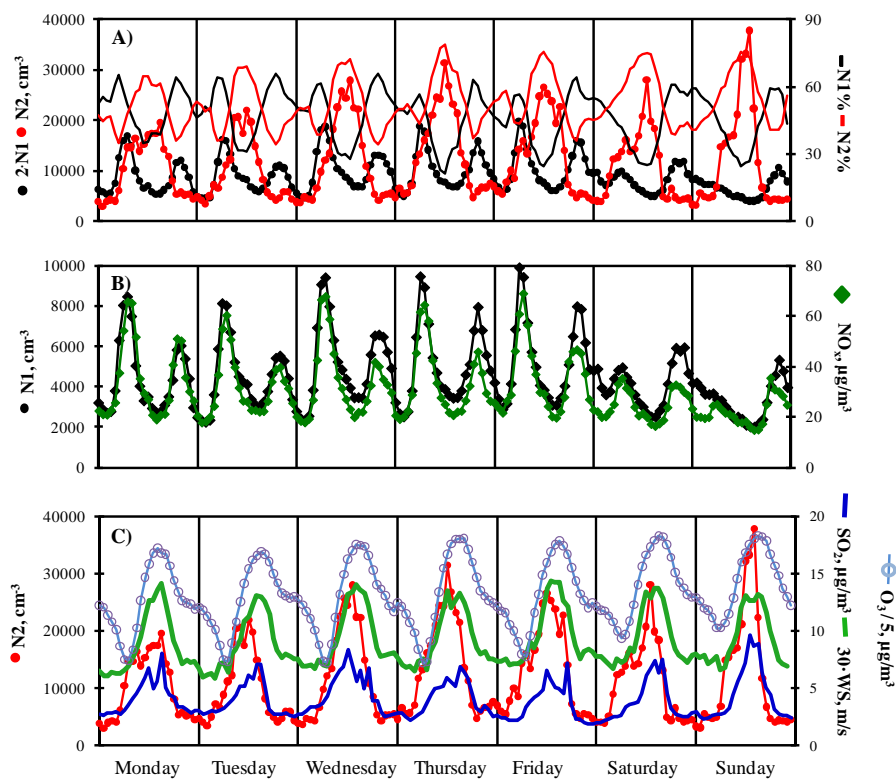
**Fig. 5.** Hourly average values of the particle number  $N$  versus BC particle concentrations at different times of the day in Huelva city. S1 and S2 indicate the lines of minimum and maximum slopes which contain the  $N$ -vs.-BC data.

period, the  $N$  versus BC data set is grouped between two well defined borders with slopes S1 and S2, representing the minimum and maximum  $N/BC$  ratios, respectively (Fig. 5a). Table 1 shows the values of slopes S1 and S2 obtained in different periods of the day. During the  $\text{NO}_x$  morning peak period (06:00–09:00 h), S1 showed a value of  $6.9 \times 10^6$  particles per nanogram of black carbon (particles/ng BC) and it is interpreted as the minimum number of particles formed/emitted per each nanogram of BC emitted by vehicle exhausts. In this period, S2 showed a value of  $148 \times 10^6$  particles/ng BC. Increases in the  $N/BC$  ratio, from  $S1=6.9 \times 10^6$  particles/ng BC up to  $S2=148 \times 10^6$  particles/ng BC as maximum value, are interpreted to be caused by enhancements in the new particle formation processes during the dilution and cooling of the vehicle exhaust emissions and/or in ambient air (Casati et al., 2007; Gidhagen et al., 2005). During the evening  $\text{NO}_x$  peak period (18:00–23:00 h), S1 and S2 show values close to those observed during the morning  $\text{NO}_x$  peak hours (Table 1). From mid-morning to the afternoon period (10:00–15:00 h), S1 showed a value of  $66 \times 10^6$  particles/ngBC, which is an order of magnitude higher than that observed during the morning rush hours. This much higher number of particles per each nanogram of BC in the ambient air is attributed to the activation of an additional new particle formation mechanism (not linked to primary BC emissions). This is supported by the fact that the S1 slope is not as well defined during the 10:00–15:00 h period as during the morning  $\text{NO}_x$  peak period (06:00–09:00 h). This high  $N/BC$  ratio and the low correlation between  $N$  and BC are caused by new particle formation processes not linked to vehicle exhaust emissions.

**Table 1.** Values of the slopes S1 and S2 obtained with the methodology described by Rodríguez and Cuevas (2007). S1 and S2 are expressed as  $10^6$  particles/ng BC.

Period		S1	S2
Daily	00:00–23:00 h	4.70	356.60
Night	00:00–05:00 h	6.78	350.60
Morning	06:00–09:00 h	6.90	148.40
Mid morning to afternoon	11:00–17:00 h	66.30	356.60
Evening	18:00–23:00 h	4.70	23.16

The S1 value found during the morning  $\text{NO}_x$  peak in Huelva city ( $6.9 \times 10^6$  particles ( $>2.5$  nm)/ng BC) is close to those observed in other cities:  $4.94 \times 10^6$  particles ( $>3$  nm)/ng BC in Santa Cruz de Tenerife,  $4.69 \times 10^6$  particles ( $>10$  nm)/ng BC in Barcelona and  $4.75 \times 10^6$  particles ( $>10$  nm)/ng BC in Milan (Rodríguez and Cuevas, 2007). In Huelva the S2 slope is much higher than that observed in other cities, for example S2 in the mid-morning to afternoon period is equal to  $47 \times 10^6$  particles/ng BC in Santa Cruz de Tenerife and  $356 \times 10^6$  particles/ng BC in Huelva. This indicates “high new particle formation” activity in Huelva from mid-morning to afternoon. In fact, the  $N/BC$  ratios in Huelva ( $50$ – $150 \times 10^6$  particles/ng BC; Fig. 4d) are much higher than those observed in other cities such as Santa Cruz de Tenerife and Barcelona ( $15$ – $25 \times 10^6$  particles/ng BC; Rodríguez et al., 2008; Pérez et al., 2010).



**Fig. 6.** Hourly average values of N1 and N2 particles (expressed in terms of absolute  $\text{cm}^{-3}$  and relative contributions) and gaseous pollutant ( $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{O}_3$ ) concentrations and of wind speed for every day of the week.

### 3.4 Sources of ultrafine particles

#### 3.4.1 Components of ultrafine particles

In order to identify the sources and processes affecting ultrafine particle concentration, N was split in two components following the methodology of Rodríguez and Cuevas (2007):

$$\text{N1} = \text{S1} \cdot \text{BC} \quad (2)$$

$$\text{N2} = \text{N} - \text{N1} \quad (3)$$

where, according to the results shown in the previous section, a value of  $\text{S1} = 6.9 \times 10^6$  particles/ng BC (the N-vs.-BC slope during the morning  $\text{NO}_x$ ) was chosen. Rodríguez and Cuevas interpreted N1 as representative of “those components directly emitted in the particle phase” and “those compounds nucleating immediately after the vehicle exhaust emission” (because they are in the aerosol phase under regular ambient air conditions). Thus, N1 accounts for incomplete fuel combustion products (e.g. black carbon, long-chain organic matter compounds or PAH), condensed trace metals, unburned oil and a fraction of sulphate and organic compounds nucleating/condensing immediately after emission (as described by Kittelson, 1998; Burtscher, 2005; Arnold et al., 2006; Rose et al., 2006). The component N2 is related to those processes giving rise to the aforementioned increases in the N/BC ratio,

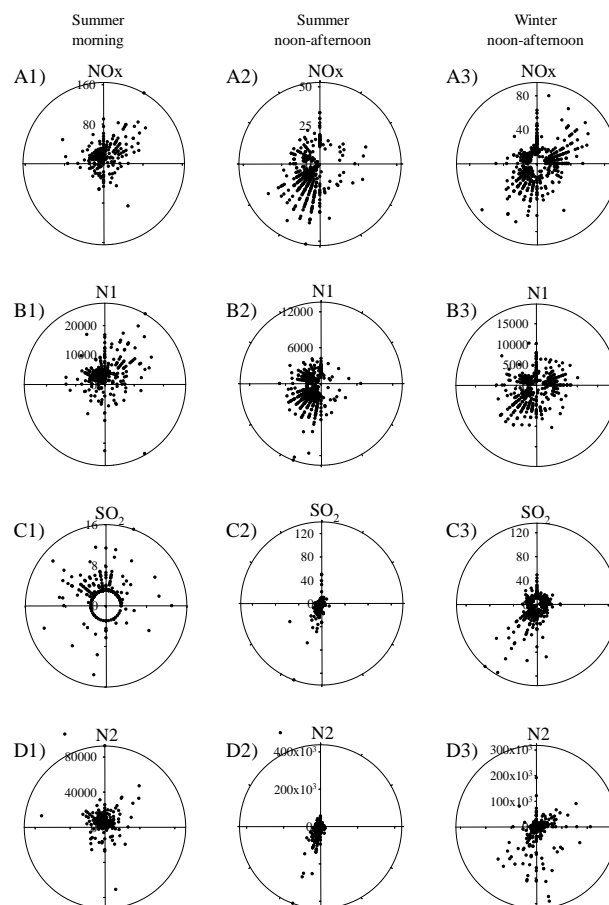
i.e. enhancement in the new particle formation rates due to increased nucleation and/or growth rates to detectable sizes ( $\geq 2.5$  nm in our case). Rodríguez and Cuevas (2007) reasoned that this enhancement in the new particle formation rates may occur in different contexts, such as “during the dilution and cooling of the vehicle exhaust emissions” (e.g. as described by Charron and Harrison, 2003; Casati et al., 2007) or in ambient air due to photochemistry (e.g. as described by Woo et al., 2001; Wehner et al., 2002). Thus, all primary particles due to vehicle exhaust are included in N1, all nucleation particles not linked to vehicle exhaust emission are included in N2, and nucleation particles formed immediately after dilution of the vehicle exhaust may contribute to both N1 and N2. Thus, this is a very useful method that provides an estimation of the fraction of the total number concentration that is linked to the “carbonaceous solid phase” emitted by vehicle exhausts (although N1 may include a fraction of compounds nucleating immediately after emission) and of the fraction linked to “nucleation mode particles”. The latter may be related to gaseous precursors emitted by different sources and should be studied site-to-site (industrial, ships, biogenic, etc.). Figure 6 shows the hourly average values of N1 and N2 for every day of the week; these results will be discussed below.



### 3.4.2 Identification of sources

In order to identify the sources and processes affecting particle number  $N$  concentration, a set of Principal Component Analyses (PCA) followed by varimax rotations were performed using 1-h average data. Because the principal components (PC) obtained depend on the number and types of variables introduced in the PCA, a number of tests were performed. Initially, only particles ( $N_1$ ,  $N_2$  and  $PM_{10}$ ) and primary gaseous pollutants ( $NO_x$  and  $SO_2$ ) were introduced. In a second step, different combinations of meteorological parameters, “road-traffic intensity/wind speed” ratio and ozone were chosen. Moreover, PCA were performed separately with the data collected during the morning rush hours (06:00–09:00 h) and during the noon-afternoon period (11:00–17:00 h). Winter and summer periods were also segregated. Thus, about 40 PCAs were performed. For the sake of brevity, only four examples are shown (Table 2). Correlations between meteorological parameters and PC including particle number concentrations were observed only in some cases. The following PCs were persistently observed:

- a principal component (PC-1) positively correlated with  $N_1$ ,  $NO_x$ ,  $PM_{10}$  and the “road-traffic intensity/wind speed” ratio was observed in the morning both in winter and in summer. This profile supports the interpretation of the  $N_1$  origin described above: mostly carbonaceous material directly emitted in the particle phase and compounds nucleating/condensing immediately after the emission (Rose et al., 2006). Thus, this PC represents a fraction of the particles emitted by vehicle exhausts (mostly the solid phase). Observe in Fig. 8b and f that  $N_1$  and  $NO_x$  reach their highest concentrations during the morning and evening rush hours. These exhaust emissions and road-dust resuspension account for the  $PM_{10}$  association in this PC. Association with temperature and/or relative humidity was not observed due to the primary nature of these  $N_1$  particles. This PC was also observed in the noon-afternoon of the winter period, but not in the summer probably because of the enhanced dilution conditions in the warm season.
- PC-2 in the morning was positively correlated with  $N_2$  and  $SO_2$ . This association supports the interpretation of the  $N_2$  origin described above: new particle formation by nucleation and particle growth to a detectable size ( $\geq 2.5$  nm; Arnold et al., 2006). These  $SO_2$  emissions in the morning (when this pollutant typically shows relatively low concentrations, 3–10  $\mu\text{g}/\text{m}^3$ ) are attributed to vehicle exhaust emissions (light and heavy duty engines). The fact that high  $N_2$  and  $SO_2$  concentrations are observed when the wind blows from the north (as in the case of  $N_1$  and  $NO_x$ ; Fig. 7A1 and 7B1) and the positive correlation of  $U$  and  $V$  wind components in this factor, indicates the influence of exhaust emissions from vehicles running along the northern side of



**Fig. 7.** Hourly mean values of  $N_1$  and  $N_2$  particles and of  $NO_x$  and  $SO_2$  concentrations during the summer morning (06:00–09:00 h), summer noon-afternoon and winter noon-afternoon (11:00–17:00 h) as functions of wind direction.

the ring road around Huelva city (Fig. 1 and Fig. 7C1 and 7D1). Observe in Fig. 8c that the  $N_2$  maximum in the morning is only observed in winter. The fact that solar radiation is also correlated with this factor suggests that  $SO_2$  photo-oxidation during transport from the road (where the emission takes place) to our background measurement site may enhance new particle formation rates (Pirjola, 1999).

- PC-2 was also correlated with  $N_2$  and  $SO_2$  in the noon-afternoon period. In this period, the northward inland breeze blowing favors the inland transport of the industrial  $SO_2$  plumes (emitted in the shore; Fig. 1) and the fumigations over the city. For this reason, the highest  $SO_2$  concentrations were recorded when the wind blew from the SSW ( $\sim 185^\circ$ ), where the Cu-smelter and refinery plants are located (Fig. 7C2 and C3). The fact that concentrations of  $SO_2$  during the noon-afternoon were higher during winter than during summer is associated with the seasonal change in the sea breeze blowing. In

**Table 2.** Factor loading of the Principal Components Analysis (followed by a varimax rotation) obtained with hourly data in the morning (06:00–09:00 h) and noon-afternoon (11:00–17:00 h) in summer (June–September 2008) and winter periods (January–March 2009). Factor loadings with absolute values  $\geq 0.6$  are in bold. RAD: Solar radiation; VEHICLES/WS: Number of vehicles/hour;  $U$ : zonal component of wind (west–east);  $V$ : meridional component of wind (south–north). #NI: variable non included in this example.

	MORNING		WINTER		SUMMER		
			PC1	PC2	PC1	PC2	
			vehicle	vehicle	vehicle	vehicle	
			exahust-1	exahust-2	exahust-1	exahust-2	
N1			<b>0.926</b>	0.035	<b>0.939</b>	0.077	
N2			0.256	<b>0.675</b>	0.266	<b>0.704</b>	
NO <sub>x</sub>			<b>0.853</b>	0.319	<b>0.908</b>	0.061	
SO <sub>2</sub>			0.156	<b>0.667</b>	−0.156	<b>0.806</b>	
RAD			−0.048	<b>0.703</b>	−0.286	<b>0.724</b>	
O <sub>3</sub>			#NI	#NI	#NI	#NI	
VEHICLES/WS			<b>0.756</b>	−0.032	<b>0.681</b>	−0.124	
PM <sub>10</sub>			<b>0.670</b>	0.171	<b>0.830</b>	−0.149	
$V$			−0.014	0.551	#NI	#NI	
$U$			0.378	0.534	#NI	#NI	
$T$			#NI	#NI	#NI	#NI	
HR			#NI	#NI	#NI	#NI	
var, %			38	17	48	23	

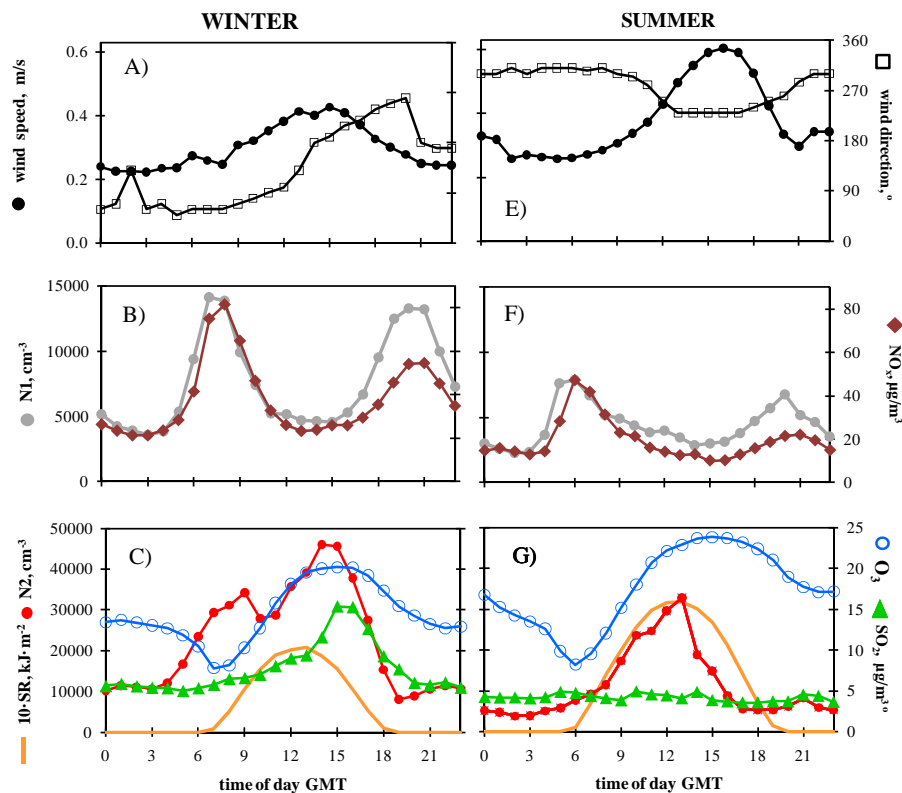
  

	NOON-AFTERNOON		WINTER		SUMMER			
			PC1	PC2	PC3	PC1	PC2	PC3
			vehicle	industrial	Gas	Urban plume+	industrial	meteo
			exahust-1		photochemistry	O <sub>3</sub> formation		
N1			<b>0.687</b>	0.539	−0.053	<b>0.745</b>	0.159	−0.043
N2			0.047	<b>0.609</b>	0.147	−0.039	<b>0.857</b>	−0.114
NO <sub>x</sub>			<b>0.702</b>	0.488	0.057	0.573	0.562	0.047
SO <sub>2</sub>			0.114	<b>0.635</b>	0.195	0.106	<b>0.805</b>	0.003
RAD			−0.012	−0.066	<b>0.794</b>	−0.108	0.431	0.533
O <sub>3</sub>			−0.460	0.354	<b>0.634</b>	<b>0.797</b>	−0.092	0.281
VEHICLES/WS			<b>0.771</b>	−0.152	0.004	−0.218	0.097	−0.323
PM <sub>10</sub>			0.135	<b>0.796</b>	0.089	0.594	0.464	−0.267
$U$			0.408	0.076	0.555	0.338	0.475	0.113
$V$			0.100	<b>−0.781</b>	0.146	−0.258	−0.066	<b>0.661</b>
$T$			0.043	0.511	<b>0.706</b>	0.285	0.044	<b>0.763</b>
HR			−0.042	−0.016	<b>−0.872</b>	−0.056	0.003	<b>−0.888</b>
var, %			13	31	20	12	26	20

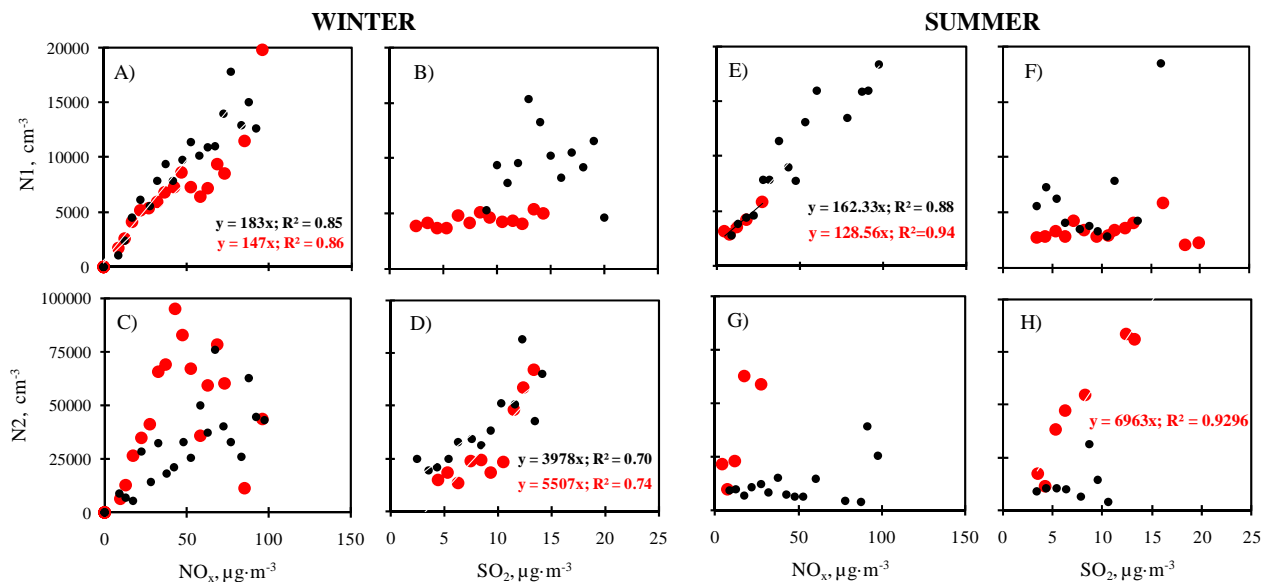
wintertime, the change in wind direction from NNE at night to S during the afternoon occurred via the east (clockwise; Fig. 8a). This resulted in frequent fumigations of the plumes over the city and in high SO<sub>2</sub> concentrations in the 11:00–17:00 h period (Fig. 8c). In summer, the night (NW) to afternoon (SW) change in wind direction occurred via the west (counterclockwise) and consequently the plumes were very frequently transported westward without impacting on the city. For this reason, the afternoon SO<sub>2</sub> and N2 concentrations were lower in summer than in winter (Fig. 8c and 8g). This association between southern winds and N2 and SO<sub>2</sub> is clearly observed in PC-2 in winter (Table 2),

– PC-3 represents relationships between meteorological parameters and O<sub>3</sub>.

In order to quantify the relationship between “N1 and N2” and “NO<sub>x</sub> and SO<sub>2</sub>”, an analysis with data averaged in intervals of 25 µg NO<sub>x</sub>/m<sup>3</sup> (0–25, 25–50,...) and 1 µg SO<sub>2</sub>/m<sup>3</sup> (0–1, 1–2,...) was performed in order to reduce the other influencing parameters (Fig. 9). Observe that N1 showed high linearity with NO<sub>x</sub> (Fig. 9a and e) but not with SO<sub>2</sub> (Fig. 9b and f). Similarly, N2 did not show correlation with NO<sub>x</sub> (Fig. 9c and g), but exhibited high linearity with SO<sub>2</sub> (Fig. 9d and h). The fact that no correlation between N2 and SO<sub>2</sub> is observed during the summer morning is attributed to the influence of temperature on the condensation processes that result



**Fig. 8.** Hourly average values of N1, N2, NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub> concentrations, of wind speed and direction and of solar radiation (SR) in Huelva in winter and summer.



**Fig. 9.** Concentrations of N1 and N2 particles versus NO<sub>x</sub> and SO<sub>2</sub> during the morning (black circles) and noon-afternoon (red circles) in winter and summer. Data are averaged in 25 µgNO<sub>x</sub>/m<sup>3</sup> interval widths (0–25, 25–50, ...) and every 1 µgSO<sub>2</sub>/m<sup>3</sup> interval width (0–1, 1–2, 2–3, ...).

**Table 3.** Mean number concentrations and contributions of N1 and N2 in different periods during the whole study period, in winter and in summer.

		N	N1	N2	N1	N2
		cm <sup>-3</sup>	cm <sup>-3</sup>	cm <sup>-3</sup>	%	%
Summer 2008						
Night	00:00–05:00 h	8582	3660	4922	42	58
Morning	06:00–09:00 h	16 228	5248	10 979	35	65
Afternoon	10:00–15:00 h	34 686	3299	31 387	19	81
Evening	18:00–23:00 h	11 175	5203	5972	48	52
All day	00:00–23:00 h	17 185	4183	13 002	36	64
Winter 2009						
Night	00:00–05:00 h	15 912	4915	10 997	38	62
Morning	06:00–09:00 h	38 734	9906	28 828	34	66
Afternoon	10:00–15:00 h	40 639	4722	35 917	22	78
Evening	18:00–23:00 h	20 286	10 303	9983	50	50
All day	00:00–23:00 h	28 979	7088	21 504	36	64
Summer 2009						
Night	00:00–05:00 h	11 542	4890	6652	46	54
Morning	06:00–09:00 h	26 688	7262	19 069	36	64
Afternoon	10:00–15:00 h	41 220	3634	36 698	20	80
Evening	18:00–23:00 h	11 173	4950	6233	49	51
All day	00:00–23:00 h	21 558	4874	16 263	38	62

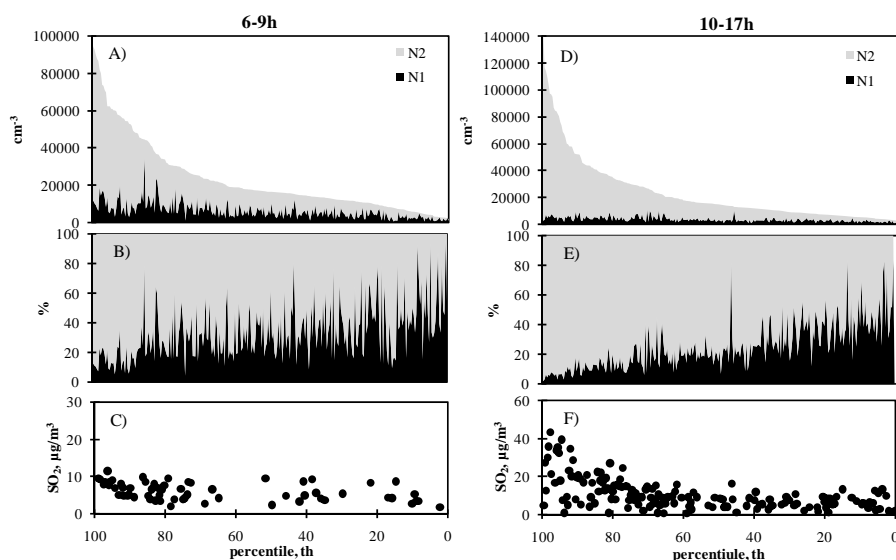
in cluster growth to detectable sizes,  $\geq 2.5$  nm (Gidhagen et al., 2005; Casati et al., 2007). This is supported by the fact that the N2 versus SO<sub>2</sub> slope for the period 06:00–09:00 h showed a decreasing trend with temperature (slope = 3258 for  $T$ : 0.0–3.5 °C, 2874 for  $T$ : 3.5–4.5 °C, 857 for  $T$ : 4.5–5.5), and no correlation between N2 and SO<sub>2</sub> was observed for temperatures  $> 6$  °C. Observe that N2 showed a morning maximum (linked to vehicle exhaust emissions) in winter (Fig. 8c) but not in summer (Fig. 8g). The fact that the correlation between N2 and SO<sub>2</sub> is observed from low to high SO<sub>2</sub> concentrations, suggests that N2 is predominantly influenced by the SO<sub>2</sub> plume dispersion scenarios (Fig. 9d and h). Similarly, N1 is dominated by vehicle exhaust products (Fig. 9a and 9e).

### 3.5 Contributions to ultrafine particle concentrations

Figure 6 shows the hourly average values of N1, N2, NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub> concentrations and of wind speed for every day of the week. Table 3 shows the average values of N and the contributions of N1 and N2. The highest N1 concentrations were recorded during the morning rush hours on working days, when ultrafine particles (N) are mostly attributed to vehicle exhaust emissions. In this period, when N showed an average value of  $\sim 27\,000$  cm<sup>-3</sup>, the contributions of N1 and N2 accounted for 35% and 65% of N, respectively.

The weekly evolution of N2 is significantly different to that of N1. High N2 concentrations are observed during the period when the sea breeze is blowing inland. Observe that the increase in N2 concentrations (from 11:00 h) is correlated with the increase in wind speed and in SO<sub>2</sub> and O<sub>3</sub> concentrations (Fig. 6c). The parallel between N2 and solar radiation suggests the active role of SO<sub>2</sub> photo-oxidation in new particle formation during the inland transport of SO<sub>2</sub> plumes (Fig. 8c and 8g). During this 11:00–17:00 h period, when N typically shows values of  $\sim 39\,000$  cm<sup>-3</sup>, N2 accounted for 80% of N.

In order to quantify the contributions of N1 and N2 to N, data were classified from the highest to lowest values of N (100th to 1st percentile). The contributions of N1 and N2 to N are highlighted in black and grey, respectively (Fig. 10a and e). It can clearly be observed that increasing N concentrations are associated with much higher increases in N2 than in N1 concentrations (Fig. 10a and d). Thus, during N2 events representing the 80th percentile, N1 only accounted for about 20% of N during the morning rush hours and for 10% of N during the 11:00–17:00 h period (Fig. 10b and e). The fact that ultrafine particles may reach higher concentrations during the 11:00–17:00 h period (up to  $130\,000$  cm<sup>-3</sup>) than during the morning (up to  $90\,000$  cm<sup>-3</sup>) is prompted by the much higher contributions of N2. Figure 10c and f show the SO<sub>2</sub> concentrations associated with each N value plotted in Fig. 10a and d. These results evidence the important



**Fig. 10.** Hourly average values of total number concentration ( $N = N1 + N2$ ) classified from the highest (100th) to the lowest (0th) value. The contributions of N1 (black) and N2 (grey) to N, in absolute ( $\text{cm}^{-3}$ ; **A** and **D**) and relative (%) concentrations, are highlighted. The  $\text{SO}_2$  concentrations associated with the decreasing N values (from 100th to 0th) are plotted (**C** and **F**).

involvement of the  $\text{SO}_2$  emissions in the ultrafine particle pollution several (7–14) kilometers downwind. Observe in Fig. 10c and f that increasing N values from the 1st to 100th percentile are associated with increasing  $\text{SO}_2$  concentrations from 10 to  $20 \mu\text{g}/\text{m}^3$  in the morning and from about 5 to  $50 \mu\text{g}/\text{m}^3$  in the 11:00–17:00 h period. This increasing trend with ultrafine particles was not observed in  $\text{NO}_x$  (not shown).

#### 4 Summary and conclusions

Most studies on ultrafine particles and air quality have focused on vehicle exhaust emissions and on new particle formation in ambient air mostly under “clean air” conditions. In this article we have presented a study of the processes influencing ultrafine particle concentrations in an urban coastal area where significant emissions of gaseous particle precursors take place (Huelva, SW Spain). These emissions are mostly linked to industrial activities. The study is based on measurements of the number of particles coarser than 2.5 nm (N), particulate black carbon (BC), gaseous pollutants and meteorological parameters taken over 17 months in an urban background site located 7–14 km from the industrial area.

By using the minimum slope observed in the N versus BC plot ( $6.9 \times 10^6$  particles/ng BC), N was split into two components:  $N = N1 + N2$ . Component N1 shows high values during the morning and evening rush hours on working days, and it is highly correlated with the “road-traffic intensity/wind speed” ratio. This component (N1) correlates with  $\text{NO}_x$ , the light-absorption coefficient due to carbonaceous material and elemental carbon determined by analysis

on filter. In contrast, it does not correlate with  $\text{SO}_2$ . N1 accounts for vehicle exhaust emissions of carbonaceous material and may also include compounds nucleating/condensing immediately after emission. Component N2 shows a behavior well differentiated from that of N1. It is correlated with  $\text{SO}_2$  and accounts for new particle formation due to nucleation and rapid particle growth to detectable sizes ( $\geq 2.5$  nm). Every day, the highest N2 concentrations were recorded during the 11:00–17:00 h period, when the sea breeze blowing inland resulted in simultaneous increases in wind speed and in the concentrations of N2,  $\text{SO}_2$  and  $\text{O}_3$ . This behavior is attributed to new particle formation in the inland sea breeze airflow due to photo-oxidation of gaseous aerosol precursors and the subsequent nucleation/condensation of oxidized vapors, with  $\text{SO}_2$  being a key component. In wintertime, an additional secondary N2 maximum was observed during the morning rush hours, with this being attributed to vehicle exhaust emissions containing sulfur compounds. During the morning rush hours, when ultrafine particles are attributed to vehicle exhaust emissions and about  $27\,000 \text{ cm}^{-3}$  are typically observed, the contribution of N1 and N2 accounted for 35% and 65% of N, respectively. In the 11:00–17:00 h period, when about  $39\,000 \text{ cm}^{-3}$  are typically observed, the contribution of N2 accounted for 80% of N, with these (N2) particles being attributed to new particle formation in sulfur-rich air masses. These results evidence how industrial  $\text{SO}_2$  emissions may result in ultrafine particle pollution several kilometers downwind of the emission source. Moreover, the contributions of these emissions are frequently much higher than those from vehicle exhausts.



The daily cycles of “new particle formation” during the period when the sea breeze is blowing inland described here, have recently been observed in other coastal cities located in the southern part of the European Union, such as Santa Cruz de Tenerife and Barcelona (Rodríguez et al., 2008; Pérez et al., 2010). The overall observations suggest that new particle formation seems to be favored in the inland sea breeze airflow. Moreover, new particle formation rates are enhanced under high emission rates of gaseous aerosol precursors in the shore (ships, power plants and/or industrial states). The fact that the N/BC ratios in Huelva during the period when the sea breeze is blowing inland (N/BC:  $50\text{--}125 \times 10^6$  particles/ng BC) are much higher than those observed in Santa Cruz de Tenerife and Barcelona (N/BC:  $15\text{--}25 \times 10^6$  particles/ng BC in both cities) is attributed to the much higher emission rates of aerosol precursors in this highly industrialized region. These observations contrast with those made in Central – Northern Europe, where ultrafine particles in urban air are mostly attributed to vehicle exhaust emissions, with new particle formation in urban air being observed during some summer periods (e.g. Wehner and Wiedensohler, 2003).

Finally, it is also interesting to highlight that the method used here to segregate the particle number into components, N1 and N2, allows accounting for particles linked to vehicle exhaust emissions and particles originated from other sources and/or processes. This offers a great potential for forthcoming source apportionment studies and for air quality assessment for human health protection.

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