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

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Studies on ultrafine particles and air quality have mostly focused on vehicle exhaust emissions and on new particle formation in “clean” ambient air. Here we present a study of the processes contributing to ultrafine particle concentrations in an urban coastal area (Huelva, SW Spain) 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 11–17 h period, under the sea breeze regime, when photochemical activity resulted in high O₃ levels and 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. SO₂)” 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 formation” during the period when the inland sea breeze is blowing period seem to be a feature of ultrafine particles in coastal areas of South-west 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

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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 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 PM₁₀ and PM_{2.5} (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 85% 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):

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- *Primary vehicle exhaust emissions.* These particles show bimodal size distribution, with a nucleation (<30 nm) and a soot mode (50–100 nm). The nucleation mode is attributed to binary H₂O–H₂SO₄ nucleation and subsequent growth by condensation of sulfuric acid and/or hydrocarbons during the dilution and cooling of the exhaust emissions (Burtcher, 2005; Arnold et al., 2006). A fraction of the nucleation mode material is semi-volatile and its formation rate depends on the dilution conditions and 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).
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- *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 (≥ 2.5 nm, according to the technology currently available). 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 (≥ 2.5 nm). 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).
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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 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 SO₂ 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_{2.5} 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

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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., 2008; Fernández-Camacho, 2010), the most significant industrial activities in Punta del Sebo include: (i) a Cu-smelter plant whose SO₂, H₂SO₄, As, Sb, Pb, Zn and Sn emissions are well documented, and (ii) phosphoric acid production plants, which are a source of atmospheric NH₄⁺ and Na phosphate,

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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 SO₂ 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, SO₂, NO_x, NH₃, Ni, V and particulate matter. Finally, ship emissions may occur in the harbor and in the bay of Huelva. This is a transit region for ships sailing to/from the Strait of Gibraltar, which ~80 000 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. SO₂).

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 PM₁₀ concentrations, gaseous pollutant concentrations (NO_x, SO₂ and O₃, 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.

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2.2.1 Particles

Number concentration of particles coarser than 2.5 nanometers (N) was monitored by using an Ultrafine Condensation Particle Counter (UCPC, TSI™, model 3776). The instrument records average data at 1-min intervals when operating 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 85% 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 PM₁₀ 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 λ=630 nm (σ_{ap} in M m⁻¹ units) taken with the MAAP by applying Eq. (1) (Petzold and Schönlinner, 2004):

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

where σ is the “specific aerosol absorption coefficient” (expressed in m²/g units). In order to determine “σ”, samples of PM₁₀ particles were collected in a high volume (68 m³/h) sampler. In these PM₁₀ samples, elemental carbon (EC) concentrations were determined by analysis in the laboratory. These were performed by means of the Thermo Optical 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_{2.5} sampling was occasionally performed to determine the PM_{2.5}/PM₁₀ ratio for BC.

Concentrations of PM₁₀ particles were determined by means of a beta attenuation monitor and a sampler for collecting PM₁₀ samples on filter media. Daily average gravimetric PM₁₀ concentrations were determined by filter weighing after conditioning (20 °C and 50% RH). Gravimetric equivalent hourly average PM₁₀ concentrations were determined by multiplying the PM₁₀ readings of the beta monitor by the “correction

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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

5 The following complementary measurements were performed: (i) concentrations of SO₂, NO_x and O₃ were monitored using standard procedures following the reference methods of the European air quality directives, (ii) road-traffic intensity (number of vehicles 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
10 humidity, pressure and global radiation).

3 Results and discussion

3.1 Absorbing aerosols

The specific aerosol absorption coefficient σ (expressed in m²/g units) was determined by comparing the absorption coefficient σ_{ap} measured by the MAAP with the elemental carbon (EC) concentrations determined by the Sunset analysis of the PM₁₀ samples. An average value of $\sigma = 10.31 \pm 0.25$ m²/g was obtained (Fig. 2a). This σ value is within the range of those typically observed in previous studies (2–25 m²·g⁻¹; Bond and Bergstrom, 2006). Because of the low σ values typically associated with other potentially absorbing species, such as mineral dust (0.01–0.02 m²·g⁻¹; Alfaro et al., 2004) or organic aerosols (e.g. humic-like substances $\sigma \sim 0.03$ m²·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. 3b, discussed below), we assume that the measured absorption coefficient is entirely due to absorption by EC. Observe in Fig. 2b that about the 75% of the EC mass in PM₁₀ occurs in the fine (PM_{2.5}) fraction.

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3.2 Regular daily evolution

Figure 3 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. 3b 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. 3d).

The mean value of the ≥ 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 Pittsburgh for ~ 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 ≥ 3 nm particles; Wehner et al., 2002; Shi et al., 1999). One of the most important features of the ≥ 2.5 nm particles in Huelva is their regular daily evolution. In most urban areas, the number of ≥ 3 nm particles reaches a maximum mostly during the morning rush hours (e.g., Leipzig, Santa Cruz

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de Tenerife) due to vehicle exhaust emissions. In contrast, the maximum concentrations of ≥ 2.5 nm particles in Huelva are reached during the afternoon (12–14 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 4 shows the N versus BC scatter plots for different periods of the day (0–23 h, 6–9 h, 10–15 h and 18–23 h). It can be observed that at any 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. 4a). Table 1 shows the values of slopes S1 and S2 obtained in different periods of the day. During the NO_x morning peak period (6–9 h), S1 showed a value of $6.9 \cdot 10^6$ 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 $148 \cdot 10^6$ particles/ng BC. Increases in the N/BC ratio, from $S1 = 6.9 \cdot 10^6$ particles/ng BC up to $S2 = 148 \cdot 10^6$ 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 NO_x peak period (18–23 h), S1 and S2 show values close to those observed during the morning NO_x peak hours (Table 1). From mid-morning to the afternoon period (10–15 h), S1 showed a value of $66 \cdot 10^6$ particles/ng BC, 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

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supported by the fact that the S1 slope is not as well defined during the 10–15 h period as during the morning NO_x peak period (6–9 h).

The S1 value found during the morning NO_x peak in Huelva city ($6.9 \cdot 10^6$ particles (>2.5 nm)/ng BC) is close to those observed in other cities: $4.94 \cdot 10^6$ particles (>3 nm)/ng BC in Santa Cruz de Tenerife, $4.69 \cdot 10^6$ particles (>10 nm)/ng BC in Barcelona and $4.75 \cdot 10^6$ 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 $47 \cdot 10^6$ particles/ng BC in Santa Cruz de Tenerife and $356 \cdot 10^6$ 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 – $150 \cdot 10^6$ particles/ng BC; Fig. 3d) are much higher than those observed in other cities such as Santa Cruz de Tenerife and Barcelona (15 – $25 \cdot 10^6$ particles/ng BC; Rodríguez et al., 2008; Pérez et al., 2010).

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):

$$N1 = S1 \cdot BC \quad (2)$$

$$N2 = N - N1 \quad (3)$$

where, according to the results shown in the previous section, a value of $S1 = 6.9 \cdot 10^6$ particles/ng BC (the N-vs-BC slope during the morning 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.

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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 (≥ 2.5 nm). Rodríguez and Cuevas 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, 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” (although N1 may include a fraction of compounds nucleating immediately after emission) and of the fraction that is linked to “nucleation mode particles”. Figure 5 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 (N1, N2 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 (6–9 h) and during the noon-afternoon period (11–17 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). Two PC were persistently

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observed in the morning (Table 2):

- a principal component 1 (PC-1) positively correlated with N1, NO_x, PM₁₀ and the “road-traffic intensity/wind speed” ratio was observed. This profile supports the interpretation of the N1 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. 7b and f that N1 and NO_x reach their highest concentrations during the morning and evening rush hours. These exhaust emissions and road-dust resuspension account for the PM₁₀ association in this PC.
- PC-2 is positively correlated with N2 and SO₂. This association supports the interpretation of the N2 origin described above: new particle formation by nucleation and rapid particle growth to a detectable size (≥ 2.5 nm; Arnold et al., 2006). These SO₂ 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 N2 and SO₂ concentrations are observed when the wind blows from the north (as in the case of N1 and NO_x; Fig. 6A1 and B1), indicates the influence of exhaust emissions from vehicles running along the northern side of the ring road around Huelva city (Figs. 1 and 6c1,d1). Observe in Fig. 7c that the N2 maximum in the morning is only observed in winter. The fact that solar radiation is also correlated with this factor suggests that SO₂ 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).

Because the industrial areas and harbor are located (7–14 km) to the south of Huelva city (Fig. 1), the northward inland breeze blowing during the afternoon favors the inland transport of the SO₂ plumes over the city and the mixing of urban and industrial pollutants. These fumigations and the results of the PCA showed some differences between

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summer and winter owing to differences in the sea breeze dynamic between the two seasons. In wintertime, the change in wind direction from NNE at night to S during the afternoon occurred via the east (clockwise; Fig. 7a). This resulted in frequent fumigations of the plumes (from industrial and maritime ship activities) over the city, giving rise to high SO₂ concentrations during the 11–17 h period (Fig. 7c). 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 SO₂ concentrations were lower in summer than in winter (Fig. 7c and g). The highest SO₂ concentrations were recorded when the wind blew from the SSW (~185°), where the Cu-smelter and refinery plants are located (Fig. 6C2 and C3). In the PCA performed during the 11–17 h period (Table 2):

- the influence of the SO₂ plumes is observed in the PC-1 both in winter and summer. In wintertime it seems to be mixed with light-absorbing particles (N1) and NO_x, both associated with combustion emissions. This mixing may occur during the northward inland transport of the SO₂ plumes over the city conurbation,
- the association between N1 and the “number of vehicles/wind speed” ratio, which corresponds to fresh vehicle exhaust emissions of “light-absorbing carbonaceous and immediately nucleating aerosols”, is observed in PC-3 in winter and in PC-2 in summer. In winter, high N1 and NO_x concentrations are observed when the wind blew from the NE (during the NNE to S wind turn described above; Fig. 6A3 and B3), where a turn-off into the city from the motorway is located,
- an O₃-rich sea breeze blowing inland (Millán et al., 2002) is observed in PC-2 in winter and in PC-3 in summer. In this warm season this inland transport of ozone also resulted in the transport of N1 particles and NO_x from the city center to the measurement site (Fig. 6A2 and B2),
- nucleation of sulphate is clearly observed in summer in PC1.

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In order to quantify the relationship between “N1 and N2” and “NO_x and SO₂”, the analysis shown in Fig. 8 was performed. The use of data averaged in intervals of 25 μg NO_x/m³ (0–25, 25–50, ...) and 1 μg SO₂/m³ (0–1, 1–2, ...) in Fig. 8, allows variability due to other influencing parameters to be reduced. Observe that N1 showed high linearity with NO_x (Fig. 8a and e) but not with SO₂ (Fig. 8b and f). Similarly, N2 did not show correlation with NO_x (Fig. 8c and g), but exhibited high linearity with SO₂ (Fig. 8d and h). The fact that no correlation between N2 and SO₂ is observed during the summer morning is attributed to the influence of temperature on the condensation processes that result in cluster growth to detectable sizes, ≥2.5 nm (Gidhagen et al., 2005; Casati et al., 2007). This is supported by the fact that the N2 versus SO₂ slope for the period 6–9 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 °C), and no correlation between N2 and SO₂ was observed for temperatures >6 °C. Observe that N2 showed a morning maximum (linked to vehicle exhaust emissions) in winter (Fig. 7c) but not in summer (Fig. 7g). The fact that the correlation between N2 and SO₂ is observed from low to high SO₂ concentrations, suggests that N2 is predominantly influenced by the SO₂ plume dispersion scenarios (Fig. 8d and h). Similarly, N1 is dominated by vehicle exhaust products (Fig. 8a and e).

3.5 Contributions to ultrafine particle concentrations

Figure 5 shows the hourly average values of N1, N2, NO_x, SO₂ and O₃ 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 ~27 000 cm⁻³, 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

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that the increase in N₂ concentrations (from 11 h) is correlated with the increase in wind speed and in SO₂ and O₃ concentrations (Fig. 5c). The parallel between N₂ and solar radiation suggests the active role of SO₂ photo-oxidation in new particle formation during the inland transport of SO₂ plumes (Fig. 7c and g). During this 11–17 h period, when N typically shows values of $\sim 39\,000\text{ cm}^{-3}$, 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. 9a and e). It can clearly be observed that increasing N concentrations are associated with much higher increases in N₂ than in N₁ concentrations (Fig. 9a 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 11–17 h period (Figures 9b and e). The fact that ultrafine particles may reach higher concentrations during the 11–17 h period (up to $130\,000\text{ cm}^{-3}$) than during the morning (up to $90\,000\text{ cm}^{-3}$) is prompted by the much higher contributions of N₂. Figure 9c and f show the SO₂ concentrations associated with each N value plotted in Fig. 9a and d. These results evidence the important involvement of the SO₂ emissions in the ultrafine particle pollution several (7–14) kilometers downwind. Observe in Fig. 9c and f that increasing N values from the 1st to 100th percentile are associated with increasing SO₂ concentrations from 10 to $20\text{ }\mu\text{g}/\text{m}^3$ in the morning and from about 5 to $50\text{ }\mu\text{g}/\text{m}^3$ in the 11–17 h period. This increasing trend with ultrafine particles was not observed in 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 linked to industrial

activities and secondarily to maritime transport activities (ships). 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.

5 By using the minimum slope observed in the N versus BC plot (6.9×10^6 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 NO_x , the light-absorption coefficient due to
10 carbonaceous material and elemental carbon determined by analysis on filter. In contrast, it does not correlate with 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 SO_2 and accounts for new particle formation due to
15 nucleation and rapid particle growth to detectable sizes (≥ 2.5 nm). Every day, the highest N2 concentrations were recorded during the 11–17 h period, when the sea breeze blowing inland resulted in simultaneous increases in wind speed and in the concentrations of N2, SO_2 and 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 SO_2 being a key
20 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
25 the 11–17 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 SO_2 emissions may result in ultrafine particle pollution several kilometers downwind of the

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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 air-flow. Moreover, new particle formation rates are enhanced under high emission rates of gaseous aerosol precursors. The fact that the N/BC ratios in Huelva during the period when the sea breeze is blowing inland (N/BC: 50–100 10^6 particles/ng BC) are much higher than those observed in Santa Cruz de Tenerife and Barcelona (N/BC: 15–25 $\times 10^6$ 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 offers great potential for forthcoming source apportionment studies and for assessing air quality and human health protection.

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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	0–23 h	4.70	356.60
Night	0–5 h	6.78	350.60
Morning	6–9 h	6.90	148.40
Mid morning to afternoon	11–17 h	66.30	356.60
Evening	18–23 h	4.70	23.16

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Table 2. Factor loading of the Principal Components Analysis (followed by a varimax rotation) obtained with hourly data in the morning (6–9 h) and noon-afternoon (11–17 h) in summer (June–September 2008) and winter periods (January–March 2009). Factor loadings with absolute values higher than 0.5 are in bold. RAD: Solar radiation; VEHICLES/WS: Number of vehicles/hour. #NI: variable non included in this example.

MORNING	WINTER		SUMMER		
	PC1 vehicle exahust-1	PC2 vehicle exahust-2	exahust-1	PC1 vehicle exahust-2	PC2 vehicle
N1	0.941	0.002		0.939	0.077
N2	0.268	0.622		0.266	0.704
NO _x	0.864	0.308		0.908	0.061
SO ₂	0.156	0.764		−0.156	0.806
RAD	−0.064	0.811		−0.286	0.724
O ₃	#NI	#NI		#NI	#NI
VEHICLES/WS	0.740	0.031		0.681	−0.124
PM ₁₀	0.665	0.190		0.830	−0.149
T	#NI	#NI		#NI	#NI
HR	#NI	#NI		#NI	#NI
var, %	39	25		48	23

NOON-AFTERNOON	WINTER			SUMMER		
	PC1 industrial+ ships+ city plumes	PC2 photochemistry	PC3 vehicle exahust-1	PC1 industrial+ ships	PC2 vehicle exahust-1	PC3 urban plume+ O ₃ formation
N1	0.597	−0.080	0.645	0.024	0.634	0.597
N2	0.648	0.083	−0.107	0.911	0.075	0.012
NO _x	0.632	−0.017	0.598	0.444	−0.071	0.752
SO ₂	0.712	0.183	0.029	0.878	−0.102	0.048
RAD	−0.076	0.795	−0.012	0.209	−0.550	0.127
O ₃	0.241	0.714	−0.378	−0.141	−0.182	0.831
VEHICLES/WS	−0.145	0.008	0.868	0.120	0.839	−0.174
PM ₁₀	0.789	0.096	0.073	0.441	0.528	0.369
T	0.487	0.739	0.083	#NI	#NI	#NI
HR	−0.070	−0.853	−0.079	#NI	#NI	#NI
var, %	26	25	17	26	22	22

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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 cm ⁻³	N1 cm ⁻³	N2 cm ⁻³	N1 %	N2 %
Summer 2008						
Night	0–5 h	8582	3660	4922	42	58
Morning	6–9 h	16228	5248	10979	35	65
Afternoon	10–15 h	34686	3299	31387	19	81
Evening	18–23 h	11175	5203	5972	48	52
All day	0–23 h	17185	4183	13002	36	64
Winter 2009						
Night	0–5 h	15912	4915	10997	38	62
Morning	6–9 h	38734	9906	28828	34	66
Afternoon	10–15 h	40639	4722	35917	22	78
Evening	18–23 h	20286	10303	9983	50	50
All day	0–23 h	28979	7088	21504	36	64
Summer 2009						
Night	0–5 h	11542	4890	6652	46	54
Morning	6–9 h	26688	7262	19069	36	64
Afternoon	10–15 h	41220	3634	36698	20	80
Evening	18–23 h	11173	4950	6233	49	51
All day	0–23 h	21558	4874	16263	38	62

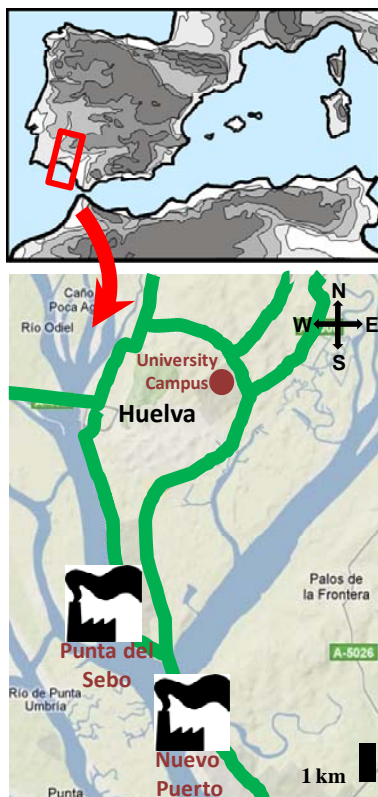


Fig. 1. Map of Huelva and the surroundings. Green lines indicate main roads and motorways around Huelva city. The two industrial areas (Punta del Sebo and Nuevo Puerto) of Huelva are highlighted.

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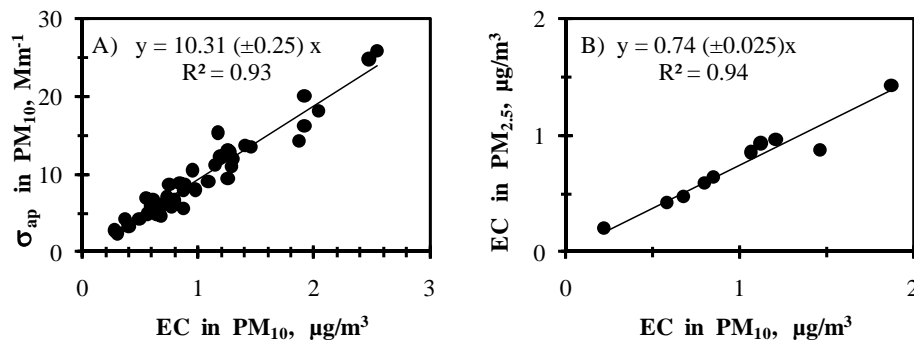
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Fig. 2. (A) absorption coefficient σ_{ap} versus EC concentrations in PM_{10} particles, (B) BC in PM_{10} versus BC $\text{PM}_{2.5}$.

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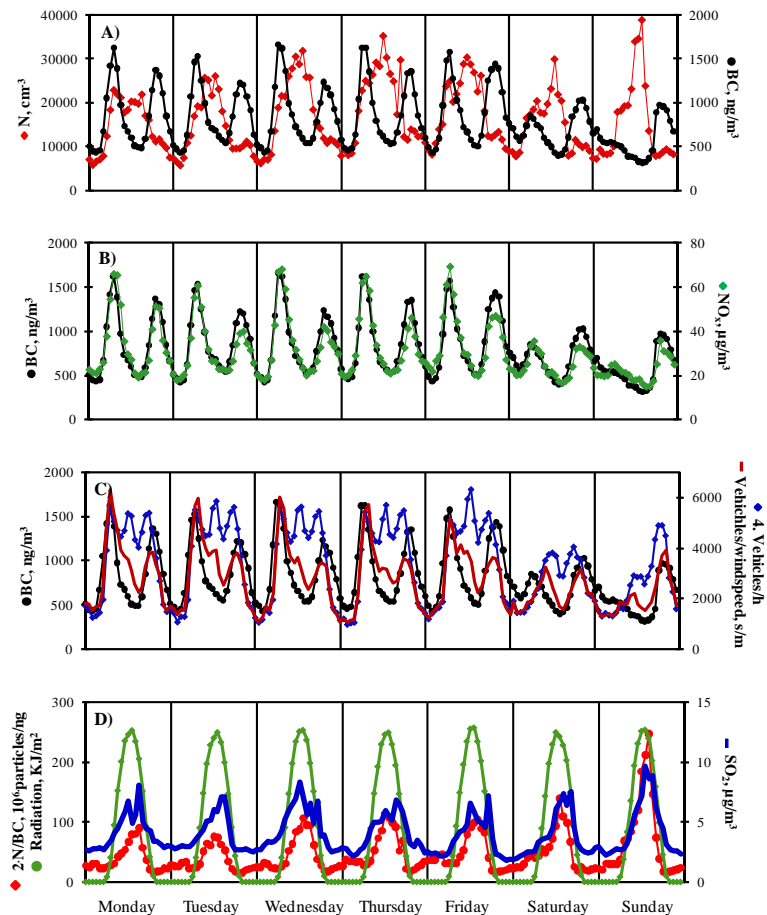


Fig. 3. Hourly average values of particles (N and BC) and gaseous pollutant (NO_x and SO_2) concentrations, and of road-traffic intensity (number of vehicles/hour), the road-traffic intensity/wind speed ratio, of the N/BC ratio and solar radiation, for every day of the week.

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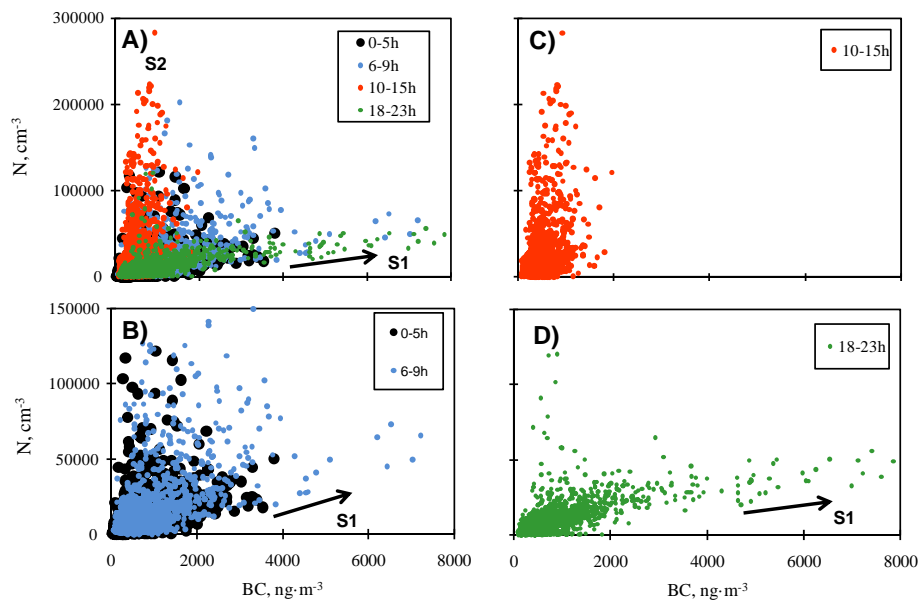


Fig. 4. Hourly average values of the particle number N versus BC particle concentrations at different times of the day in Huelva city. S1 and S2 indicate the lines of minimum and maximum slopes which contain the N -vs-BC data.

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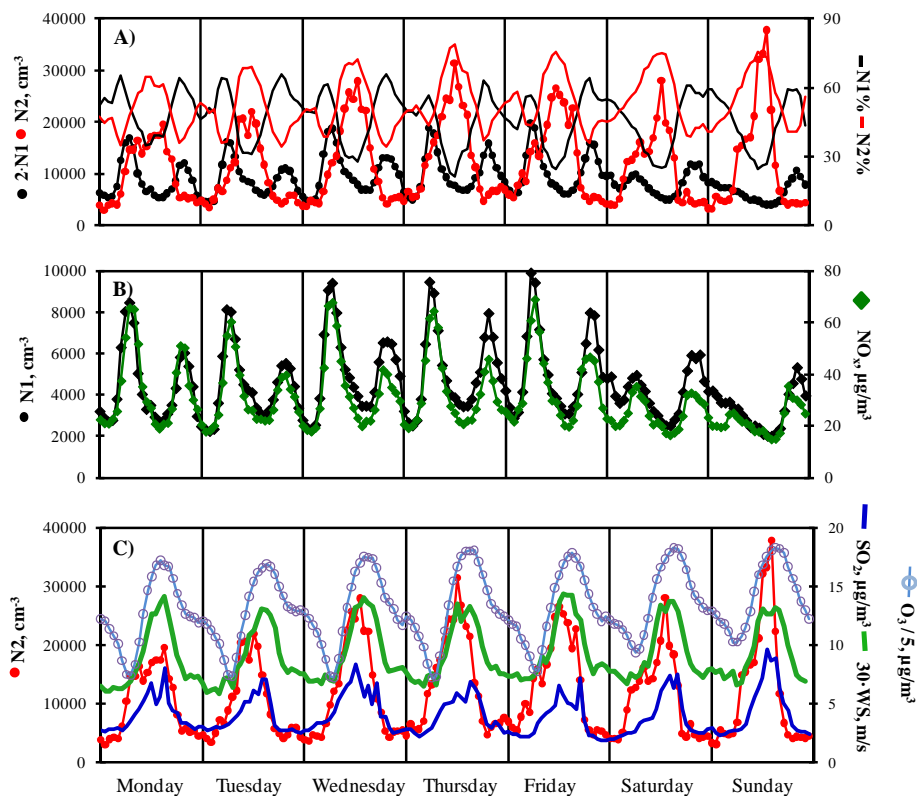


Fig. 5. Hourly average values of N1 and N2 particles (expressed in terms of absolute cm⁻³ and relative contributions) and gaseous pollutant (NO_x, SO₂ and O₃) concentrations and of wind speed for every day of the week.

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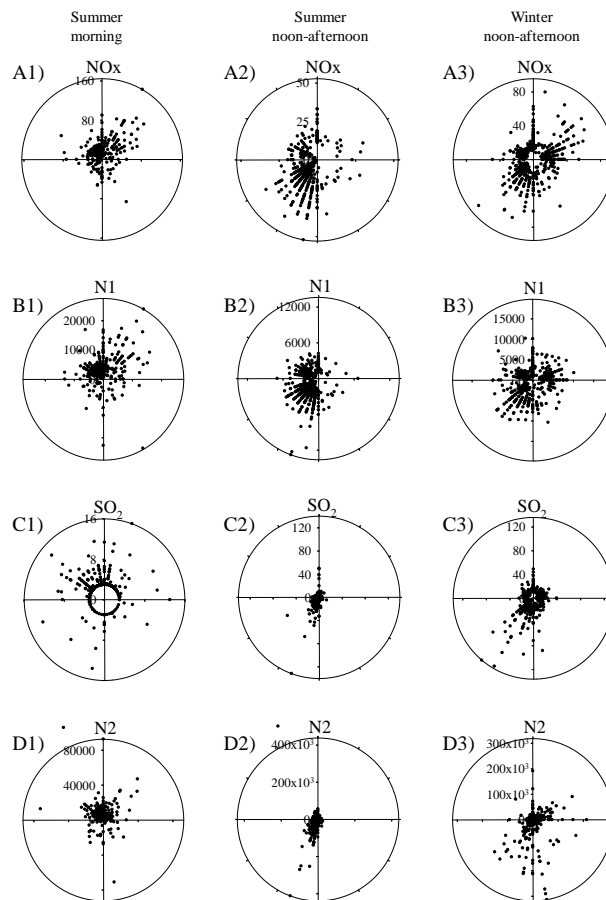


Fig. 6. Hourly mean values of N1 and N2 particles and of NO_x and SO₂ concentrations during the summer morning (6–9 h), summer noon-afternoon and winter noon-afternoon (11–17 h) as functions of wind direction.

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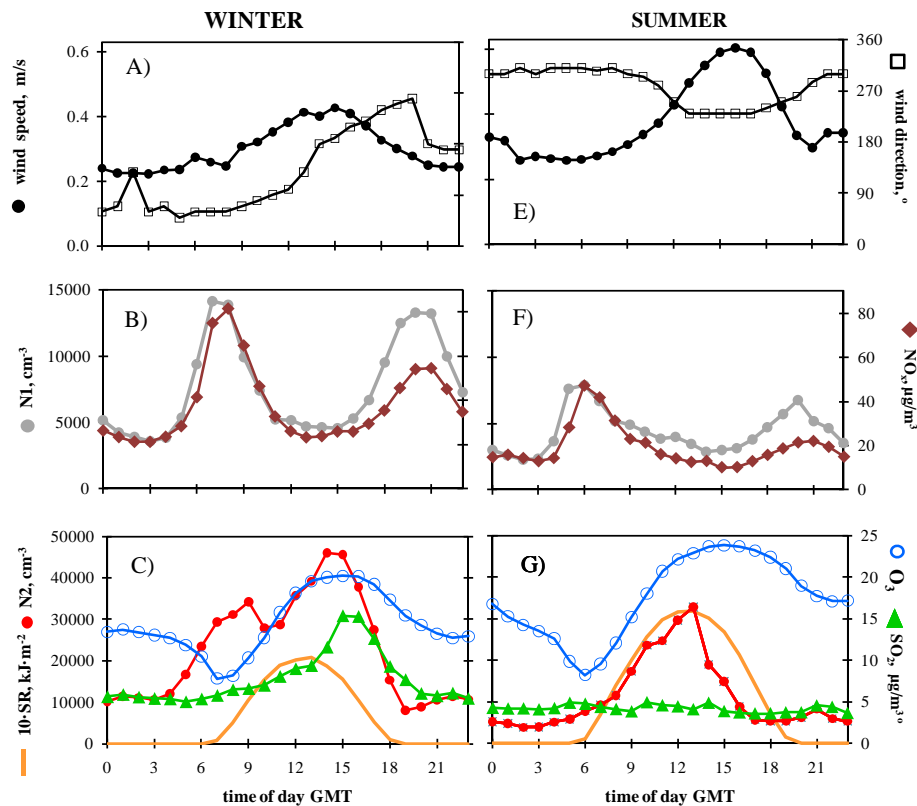


Fig. 7. Hourly average values of N₁, N₂, NO_x, SO₂ and O₃ concentrations, of wind speed and direction and of solar radiation (SR) in Huelva in winter and summer.

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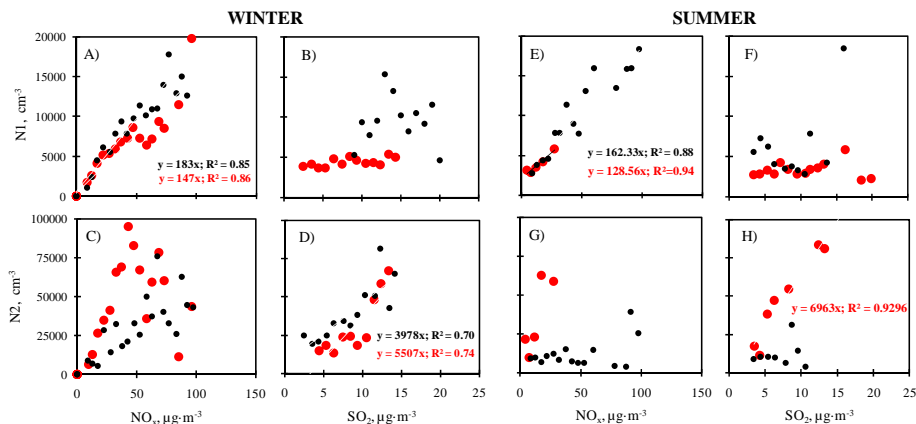


Fig. 8. Concentrations of N1 and N2 particles versus NO_x and SO_2 during the morning (black circles) and noon-afternoon (red circles) in winter and summer. Data are averaged in $25 \mu\text{g}\text{NO}_x/\text{m}^3$ interval widths (0–25, 25–50, ...) and every $1 \mu\text{g}\text{SO}_2/\text{m}^3$ interval width (0–1, 1–2, 2–3, ...).

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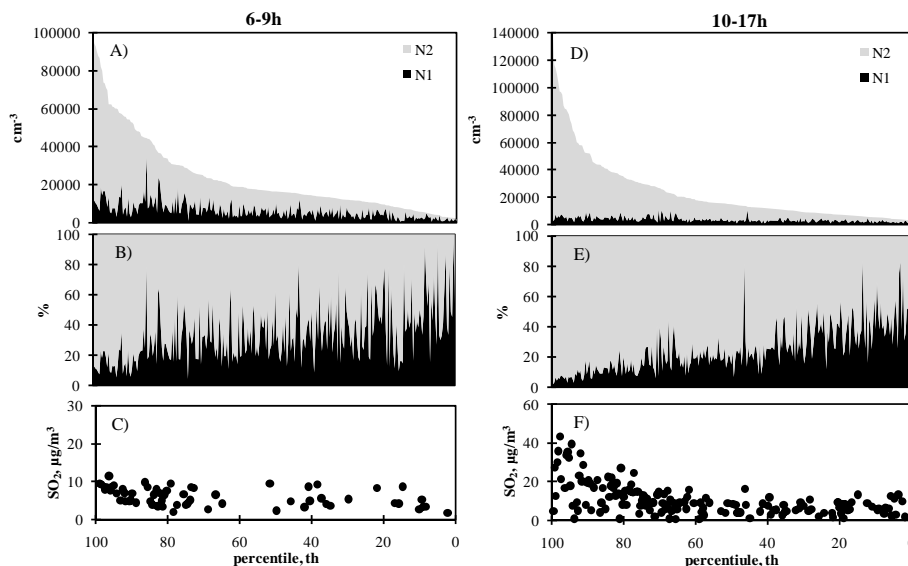


Fig. 9. Hourly average values of total number concentration ($N=N1+N2$) classified from the highest (100th) to the lowest (0th) value. The contributions of N1 (black) and N2 (grey) to N, in absolute (cm^{-3} ; **A** and **D**) and relative (%; **B** and **E**) concentrations, are highlighted. The SO_2 concentrations associated with the decreasing N values (from 100th to 0th) are plotted (**C** and **F**).

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